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Characterization of Diesel Emissions from Operation of a Light-Duty Diesel Vehicle on Alternate Source Diesel Fuels

Southwest Research Inst.
San Antonio, TX

Prepared for

Environmental Protection Agency
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by

Bruce B. Bykowski

Southwest Research Institute
6220 Culebra Road
San Antonio, Texas 78284

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Task Specification 3

EPA Project Officer: Robert J. Garbe
Task Technical Officer: Thomas M. Baines

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This report describes laboratory emissions evaluation of several alternate-source fuels in a 1980 Volkswagen Rabbit Diesel. Fuels tested included a No. 2 petroleum diesel as base, base plus coal-derived liquids, shale oil diesel fuel and jet fuel, and a blend of petroleum blend stocks with coal and shale liquids. Nine fuels were investigated in all, including the base fuel.

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ABSTRACT

This report describes laboratory emissions evaluation of several alternate-source fuels in a 1980 Volkswagen Rabbit Diesel. Fuels tested included a No. 2 petroleum diesel as base, base plus coal-derived liquids, shale oil diesel fuel and jet fuel, and a blend of petroleum blend stocks with coal and shale liquids. Nine fuels were investigated in all, including the base fuel.

Vehicle operating procedures used for test purposes included those specified in Federal Regulations (FTP)[1]* and several steady-state modes. Both regulated and unregulated gaseous and particulate emissions were measured using a CVS-PDP and dilution tunnel operating on the entire exhaust stream of the engine. DOAS odor analysis was performed on raw exhaust samples during steady-state operation. Biological response evaluation, BaP measurement, and HPLC fractionation were conducted on the organic soluble portion of the particulate. The majority of the sampling and analytical procedures used were developed during earlier EPA Contracts 68-02-2494[2], 68-03-2707[3], 68-02-1230[4,5], and 68-03-2440.[6]

* Numbers in parentheses designate references at the end of this report.

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FOREWORD

This project was conducted for the U.S. Environmental Protection Agency by the Department of Emissions Research, Southwest Research Institute. The laboratory testing phase of the project began in June 1980, and was completed in October 1981. The work was performed under EPA Contract No. 68-03-2884, Task Specification Number 3, and was identified within Southwest Research Institute as Project 05-5830-003. The scope of work defined by EPA is located in Appendix A of this report. The EPA Project Officer was Mr. Robert J. Garbe, and the Task Technical Officer was Mr. Thomas M. Baines, both of the Characterization and Technical Applications Branch, Emission Control Technology Division, Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan. The Southwest Research Institute Project Manager was Charles T. Hare, and the Project Leader and Principal Investigator was Bruce B. Bykowski.

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I. INTRODUCTION

The world's supply of crude oil is being depleted, creating incentives for discovery and utilization of alternate sources of fuel. This study was designed to determine whether or not currently available alternate-source diesel fuels would disproportionately increase regulated or currently unregulated emissions. A light-duty diesel vehicle was used for test purposes. Diesels offer more sensitive evaluation of alternate fuel effects than gasoline cars do. No exhaust aftertreatment system has to be used on diesel automobiles to meet HC and CO standards for 1982, but a catalytic converter system is used on gasoline-fueled vehicles. Changes in diesel exhaust emissions due to alternate fuels thus affect the atmosphere and the recipient directly, but the catalyst on a gasoline vehicle tends to reduce the impact of changes in emissions seen in the raw exhaust.

This study began with optimism that alternate non-petroleum fuels were available in sufficient quantities for vehicle testing. As the search went on for sources, a more realistic view surfaced. Alternate fuel research is basically still in its infancy in terms of large-volume production. Pilot plant yields are small, and the cost for pilot plant production of quantities suitable for testing in this program was prohibitive. Materials available in test quantities mostly represented first-generation alternate-source materials. As second-generation processes move from laboratories and pilot plants to larger volume production, studies such as this one could be applied to the resulting specification-quality materials for comparison purposes. It is the intent of this report, therefore, to report findings on the effects of first generation alternative-source liquids on emissions from a light-duty diesel vehicle. In many cases, these currently-available liquids did not have the specifications to run "as is". These liquids were blended with a petroleum base fuel to permit observation of any changes in emissions.

Selection of compounds and mixtures was made on the basis of availability, variety, and anticipation of second-generation compositions. Substances investigated include coal-derived liquids from both the Solvent Refined Coal (SRC-II) and Exxon Donor Solvent (EDS) processes, shale oil products, a broadcut fuel containing n-butane among other stocks, and a mixture of coal, shale and petroleum products.

II. SUMMARY AND CONCLUSIONS

The major objective of this project was to study the effects of available alternate-source fuels on exhaust emissions from one diesel vehicle, a 1980 Volkswagen Rabbit. The vehicle was operated on a Chassis dynamometer following two transient cycles (FTP and HFET), and periodically, several steady-states. Nine fuels were tested. Some of the test fuels were blends of a base No. 2 diesel and alternate-source materials, while others were fuels formulated in another study dealing with refinery modeling for alternative fuels.

One of the major challenges in performing this work was acquisition of sufficient quantities of "state-of-the-art" alternate-source materials. In most cases, these materials were still in the laboratory on pilot plant phases of production. Such processed materials were described as "second-generation" alternate-source materials. Only second-generation shale oil liquids were available in sufficient quantities for test. First-generation coal-derived liquids from two refinery processes (SRC-II and EDS), however, were available in sufficient quantities for test. It was therefore the intention of this study to report the effects of currently available alternate-source fuels on light-duty diesel emissions, and to perform detailed analyses of their compositions.

The test format was designed to produce the maximum amounts of emissions characterization information with as little vehicle operating time as possible. Physical and chemical properties of the fuels tested varied widely. Gaseous and particulate emissions collection and analyses were performed using techniques developed in earlier work.

The most important observations and conclusions reached as a result of this project (not necessarily in order) are listed below. Unless stated otherwise, all fuels will be compared to the base fuel.

1. First-generation coal-derived liquids exhibiting boiling ranges similar to petroleum-based diesel fuels could not be used "as is" in a diesel engine. Cetane numbers for the straight liquids used in this study were approximately 25 or below. Blends with petroleum-based diesel fuel were required.

2. Second-generation shale oil liquids exhibiting boiling ranges similar to petroleum-based diesel fuels had cetane numbers greater than 44, and could be used "as is" in a diesel engine.

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3. High gum levels in some blends (60 mg/100 mℓ) did not affect short-term engine operation.

4. The greatest regulated gaseous emission increases during the FTP were observed with the Broadcut and 25% SRC-II test fuels. Hydrocarbon emissions more than doubled with these two fuels. All fuels tested showed increased NO_x emissions.

5. No "total" aldehyde increases were observed during the FTP and HFET. Decreases were seen with the two coal-derived liquid blends, 25% SRC-II and 25% EDS.

6. The 25% EDS blend doubled the "total" phenol emissions during the FTP, but a large increase was not observed during the HFET. The 25% SRC-II blend did not affect phenol emissions during the FTP, but increased phenol emissions during the HFET by a factor of 14.

7. Instrumental odor analysis indicated that the Coal Case 5A and the Broadcut fuel slightly increased odor intensity in three steady-state modes.

8. Visible smoke production was generally increased with use of test fuels containing coal-derived liquids.

9. During the FTP, the 25% SRC-II blend increased the particulate mass rate 56 percent over the base fuel. However, during the HFET, the particulate rate was similar to the base. The other coal-derived fuel blends increased particulate emissions slightly. Broadcut fuel reduced particulate emissions 16 percent during the FTP, and 32 percent during the HFET.

10. Organic soluble increases of 39 percent were associated with the Broadcut and SRC-II test fuels during the FTP. During the HFET, the Broadcut fuel again increased the amount of solubles, but the SRC-II blend did not.

11. Carbon and hydrogen analysis of the organic soluble portion of the particulate matter indicated no appreciable difference between the fuels tested.

12. The boiling range determination of the organic solubles showed that the Broadcut fuel yielded the largest amount of compounds boiling under 640°C.

13. HPLC analysis on the organic solubles generated during the FTP indicated the presence of substantial amounts of PNA-type compounds from all the fuels tested. Considerable response in the transition area was observed with use of the Paraho JP-5, Broadcut, and Coal Case 5A.

14. BaP emissions were significant for all fuels tested. Levels were about 10 times higher than seen in other studies. Coal Case 5A was associated with the highest BaP emission during the FTP. Other increases were observed with the Shale Diesel Marine, Paraho JP-5, Broadcut, and 25% EDS test fuels.

15. The organic extract of the particulates from all fuels tested yielded positive Ames response, as has generally been observed in most studies. In the majority of cases, metabolic activation reduced Ames activity on all five strains, implying the presence of direct-acting mutagens. The greatest Ames responses were associated with the 25% SRC-II and the Broadcut fuel on strain TA-100.

III. TEST VEHICLE AND FUELS

The major criteria used for selection of a test vehicle were availability, and the potential to utilize a data base acquired on a similar vehicle during previous studies. Fuel selection was principally a matter of availability of alternate-source (non-petroleum) materials. Alternate-source materials were subjected to thorough analyses to establish the properties of each fuel tested in detail.

A. Test Vehicle

The vehicle chosen was a 1980 Volkswagen Rabbit. A description of the vehicle is provided in Table 1. This Rabbit was supplied to the Contractor by EPA for test purposes.

TABLE 1. DESCRIPTION OF TEST VEHICLE

Vehicle Model	Volkswagen Rabbit
Engine Model	Family D
Model Year	1980
V.I.N.	17A0926720
Engine No.	CK591126
Body Type	2-Door Hatchback
Inertia equivalent, kg (lb_m)	1021 (2250)
Transmission	5 speed manual
Displacement ℓ(in^3)	1.47 (90)
Cylinders	4
Power, kW (hp) @ rpm	(48) @ 5000
Injection System	Bosch
Combustion Chamber	Swirl Chamber
Compression Ratio	23:1
Distance on Vehicle, km[a]	2806

[a]At end of project

Baseline comparison tests were performed on the vehicles as received, using the fuel remaining in the vehicle tank from EPA tests. The test results are summarized in Table 2, with EPA and Volkswagen of America (VWOA) data.

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TABLE 2. COMPARATIVE EMISSION DATA, THREE LABORATORIES

	Average FTP Emissions			Average FET Emissions	
	VWOA[a]	EPA	SwRI	EPA	SwRI
HC, g/km	0.25	0.33	0.33	0.11	0.19
CO, g/km	0.92	0.80	0.95	0.43	0.71
NO_x, g/km	0.65	0.63	0.67	0.44	0.47
Particulate, g/km	--	0.22	0.29	0.15	0.22
Fuel, ℓ/100 km	6.14	5.88	6.22	4.35	4.89

[a]Fuel not identical to that used at EPA and SwRI

Complete test results can be found in Appendix B, pages B-2 through B-5. The dynamometer on which the tests were performed at SwRI was checked thoroughly after the tests, and the speed and load calibrations were accurate. Coast-down checks on the SwRI dynamometer indicated that the actual power absorption was slightly higher than the curve used. The difference (2.9%) was not considered sufficient to have caused the entire difference between SwRI FET results and those of EPA. Gas analyzers used for the test work were calibrated just after the runs and found to be accurate.

An additional retest was performed with comparable results. The additional retest exhausted the supply of fuel which was in the fuel tank, so further direct comparison testing between laboratories was no longer possible. A fourth, and final, comparison test using another No. 2 diesel fuel was performed. These results, along with a summary table and computer printouts, are located in Appendix B, pages B-6 through B-10. It should be noted that all comparison testing involved vehicle operation through all 5 gears, inertia set at 1077 kg (2375 lb), and actual road load of 5.1 kW (6.8 hp).

Vehicle operation during actual testing of alternative-source fuels attempted to simulate that of a 1977 Volkswagen which was used in an earlier study.(6) Inertia setting was 1021 kg (2250 lb), and actual road load was 5.4 kW (7.3 hp). During tests, only 4 of the 5 gears were used, to be consistent with the older Volkswagen's 4-speed manual transmission. It was hoped that the two Rabbits would give similar baseline results, so that the data base of the earlier study could be coupled with the results generated in this study. The results of a cross comparison between the two Rabbits is shown in Table 3. Fuels run in each Rabbit were both "National Average" No. 2 diesel, but were not from the same lot. The properties of the two fuels were almost identical. Results comparing the two Rabbits over other cycles are listed in Appendix B, page B-11.

TABLE 3. COMPARISON OF FTP[a] EMISSIONS FROM TWO VW RABBITS

Emissions	Earlier Rabbit, Fuel EM-239-F	Current Rabbit, Fuel EM-329-F
HC, g/km	0.20	0.31
CO, g/km	0.51	0.96
NO_x, g/km	0.65	0.62
Particulate, g/km	0.218[b]	0.249[c]
Fuel, ℓ/100 km	5.60	6.38

[a] 3-bag composite
[b] Based on 47 mm glass fiber filters
[c] Based on 47 mm Pallflex filters

B. Test Fuels

Acquisition of alternate-source (non-petroleum) fuels in quantities for vehicle testing was a major effort. Contact with potential sources indicated a lack of availability of several fuels which were originally intended for test. Apparently second-generation materials were available only in limited quantities from laboratory-scale processes. The term "second-generation" refers to materials derived from alternate sources with some degree of aftertreatment. Examples of aftertreatment are catalytic cracking, hydrogenation, and so forth. Cost for acquisition of these materials was extremely high. First-generation alternate-source materials were eventually found in quantities sufficient for testing. "First-generation" refers to materials derived from alternate sources with little or no aftertreatment. It was felt that reporting the effects of these available alternate-source fuels would be an important first step in building a useful data base. As second-generation materials move from the laboratory to larger-volume production, similar studies can be performed for comparison purposes.

Two second-generation alternate-source materials were available in sufficient quantities, largely due to previous interest and manufacture for U.S. Navy studies. These two materials were derived from a Paraho shale oil crude refinery run, and were identified as Paraho JP-5 and Shale Diesel Marine. Complete fuel characterization was a part of this study. Properties of these two fuels and the others tested in this study are listed in Table 4. Fuel chosen as the base fuel represented a "National Average" No. 2 diesel.

First-generation materials available were coal-derived liquids from two different refinery processes: Solvent Refined Coal (SRC-II), and Exxon Donor Solvent (EDS). Analysis of three liquids manufactured by these processes are located in Appendix B, page B-12. Due to their poor ignition quality (cetane numbers ≤ 25), vehicle operation on the straight liquids was not possible.

TABLE 4. FUEL PROPERTIES AND COMPOSITION

Substance	Base DF-2	Shale Diesel Marine	Paraho JP-5	Coal Case 5A	35% SRC-II	Broadcut Mid-Continent	25% SRC-II	25% EDS	25% EDS Naphtha
Fuel Code (EM-)	329-F	453-F	473-F	474-F	475-F	476-F	478-F	482-F	485-F
Cetane No. (D613)	50	49	45	42	31	35	38	44	45
Cetane Index (D976)	52	56	46	41	29	52	38	42	47
Gravity, °API @ 60°F	37.5	37.9	43.6	31.1	28.2	44.1	31.7	33.8	38.3
Density, g/ml @ 60°F	0.837	0.835	0.808	0.870	0.886	0.806	0.867	0.856	0.833
Carbon, wt. %	85.8	86.3	85.9	86.5	86.2	86.1	86.4	86.5	86.3
Hydrogen, wt. %	13.0	13.4	13.7	12.4	11.8	13.2	12.3	12.7	13.3
Nitrogen, ppm (oxid. pyrolysis)	48	5	<1	1600	3400	1000	2000	267	142
Sulfur (lamp), %	0.24	<0.005	0.005	0.100	0.31	0.17	0.23	0.16	0.28
Calculated H/C, numeric	1.81	1.85	1.90	1.71	1.52	1.83	1.70	1.75	1.84
Carbon No. range (G.C.)	8-24	9-20	10-15	9-24	8-20	3-24	8-20	8-20	7-20
Aromatics, vol. %	21.3	28.5	22.0	34.9	47.0	16.2	39.9	36.4	25.5
Olefins, vol. % (D1319)	1.7	2.1	2.0	1.4	0.6	0.0	1.2	0.0	0.5
Paraffins, vol. %	77.0	69.4	76.0	63.7	52.4	83.8	58.9	63.6	74.0
Viscosity, cs @100 °F (D445)	2.36	2.61	1.38	3.08	2.53	1.53	2.45	2.37	1.76
Gum, mg/100 ml (D481)	14.3	0.3	1.4	38.8	89.7[b]	23.8	30.1	60.0	13.1
Total solids, mg/ℓ	7.4	0.3			13.1		7.2	3.1	1.2
Metals in fuel, x-ray	0[a]	0[a]	0	0	0	0	9ppm Fe	0	0
Boiling Range, °C (IBP-EP, D86)	191-340	207-317	179-248	192-366	171-328	21-354	178-327	179-353	108-334
10% point	219	236	189	234	207	53	209	207	157
20% point	231	246	192	244	215	121	220	218	182
30% point	242	252	196	253	225	151	231	227	203
40% point	251	259	198	259	234	178	240	239	223
50% point	260	266	202	267	243	216	250	251	238
60% point	269	272	206	276	252	239	259	263	254
70% point	278	278	211	277	263	255	270	276	267
80% point	290	286	218	292	274	270	281	293	281
90% point	307	295	228	330	292	303	303	316	302
95% point	323	302	237	353	309	327	319	336	319
Residue, wt. % (D86)	1.3	1.0	1.5	1.5	1.0	1.0	1.0	1.5	1.5

[a] <10 ppm of Cr, Fe, Ni, Cu, Zn, and Mg; <70 ppm Pb; <100 ppm Al and Si
[b] Sample not dry after 1 hr. in steam lit block

TABLE 4 (Cont'd). FUEL PROPERTIES AND COMPOSITION

Substance	Base DF-2	Shale Diesel Marine	Paraho JP-5	Coal Case 5A	35% SRC-II	Broadcut Mid-Continent	25% SRC-II	25% EDS	25% EDS Naphtha
Fuel Code (EM-	329-F	453-F	473-F	474-F	475-F	476-F	478-F	482-F	485-F
Boiling Range, °C (IBP-EP, D2887)	104-387	118-341	157-286	140-416	103-346	24-399	129-508	128-419	72-455
10% point	197	216	175	217	158	68	193	192	139
20% point	220	237	187	238	178	123	214	210	174
30% point	239	254	195	254	196	155	232	228	197
40% point	256	265	201	264	207	196	248	243	225
50% point	268	274	210	271	219	233	259	257	249
60% point	280	285	216	284	229	251	271	273	264
70% point	292	297	224	299	240	262	285	289	279
80% point	307	307	234	315	255	280	302	305	298
90% point	330	319	244	344	278	314	321	332	314
95% point	347	325	254	367	295	342	345	356	336
Residue, wt. % (D2887)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Composition, Volume %									
Kerosene									
Petroleum	0.0	0.0	0.0	17.3	0.0	22.0	0.0	0.0	0.0
Shale JP-5	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0
Diesel									
Petroleum	100.0	0.0	0.0	66.7	65.0	23.0	75.0	75.0	75.0
Shale DFM	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Coal	0.0	0.0	0.0	16.0	35.0	6.2	25.0	25.0	25.0
Light Cycle Oil (petroleum)	0.0	0.0	0.0	0.0	0.0	5.2	0.0	0.0	0.0
LSR Naptha (petroleum)	0.0	0.0	0.0	0.0	0.0	7.4	0.0	0.0	0.0
HSR Petroleum	0.0	0.0	0.0	0.0	0.0	4.8	0.0	0.0	0.0
Shale	0.0	0.0	0.0	0.0	0.0	20.9	0.0	0.0	0.0
Coal (Simulated)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N-Butane	0.0	0.0	0.0	0.0	0.0	10.5	0.0	0.0	0.0

[a] <10 ppm of Cr, Fe, Ni, Cu, Zn, and Mg; <70 ppm Pb; <100 ppm Al and Si

Consequently, blends with the base fuel were formulated in order to permit reasonable vehicle operation, and to compare emissions from fuels derived from the two processes. Properties of these blends are listed in Table 4.

Selection of two other alternate-source materials made use of information from another study[7,8] which investigated regional refining models for fuels. This study demonstrated how syncrudes might be used to make specification products in the year 1995. Two fuel blends from the refining study were chosen to represent combinations of shale oil, coal-derived, and petroleum liquids. These two fuels were described as "Coal Case 5A", and "Broadcut Mid-Continent". Properties of these blends are listed in Table 4. It should be noted that the petroleum portion of the two blends was not the base fuel, EM-329-F. The blends were previously prepared for use in the refining model study, and were available in sufficient quantities for inclusion in our work following receipt of permission from the Department of Energy.

IV. INSTRUMENTATION AND ANALYTICAL PROCEDURES

Analytical procedures and equipment used to measure regulated and unregulated emissions are described briefly in this section. These procedures were used in earlier EPA contracts[2,3,5,6], and are routinely used in present-day emission testing.

A. Vehicle Operation and Smoke Measurements

The VW Rabbit was operated to simulate road experience on a 2-roll Model ECE-50 Clayton light-duty chassis dynamometer, of the type qualified for Federal light-duty certification.[9] Inertia and power absorption settings used for all test work on this dynamometer were set to simulate operation of an earlier model VW Rabbit tested in a previous study.[6] Discussion regarding inertia and horsepower settings was given in Section III. A. of this report.

Care was taken to insure that the vehicle's fuel system was purged properly before testing of each fuel. All test fuels were withdrawn from individual 19 liter cans. Prior to test, a 2 liter sample of test fuel was used to run the vehicle, with the return line routed to a container subsequently discarded. After this purge, the vehicle was operated for approximately 30 minutes, followed by FTP and HFET driving cycles, to remove any residuals from other fuels, and to insure that the vehicle fuel system contained only the fuel to be tested.

In order to test the Broadcut fuel, EM-476-F, an additional electric fuel pump was required at the fuel container. This pump was necessary because the Broadcut had a high vapor pressure, due to the presence of 10.5 percent n-butane. Attempting to withdraw this fuel from the can using the engine's fuel pump caused vaporization of the n-butane in the fuel line. The n-butane "bubbles" caused very poor driveability and stalling. The electric fuel pump was used to supply the fuel under pressure rather than subjecting it to pressures substantially below atmospheric.

Exhaust smoke measurements were made using an optical light-extinction smokemeter, of the type specified in Federal regulations for heavy-duty diesel engine smoke certification.[10] The smokemeter was mounted on a 51 mm (2 in.) O.D. tailpipe extension when in use. The control/readout unit for the smokemeter was mounted remote from the vehicle under test, and continuous recordings of smoke opacity were made concurrently with vehicle speed traces. Smoke measurements were made over the first 505 seconds of the cold-start FTP cycle, while the vehicle was operated on the chassis dynamometer. This procedure was developed for research purposes on an earlier EPA Contract, No. 68-03-2417.[11]

B. Regulated and Unregulated Gaseous Emissions

Regulated gaseous emissions of hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x) were collected and analyzed using procedures and equipment described in the Federal Register.[9] The method of hydrocarbon analysis was an updated version of that proposed, and eventually adopted for the 1980 Federal Register.[10] The apparatus for hydrocarbon analysis is shown schematically in Figure 1, and the components are described in Table 5.

The unregulated gaseous emissions measured were aldehydes, phenols, and odor. Aldehydes were measured using the 2,4-dinitrophenylhydrazine (DNPH) method.[2] The method consists of withdrawing a continuous sample of dilute exhaust at a rate of 0.24 m^3/hr, and bubbling the sample through glass impingers, containing DNPH in hydrochloric acid. This process forms the aldehydes' phenylhydrazone derivatives, which are eventually injected into a gas chromatograph equipped with a flame ionization detector, for separation and identification.

Phenols were measured using the ether extraction procedure.[2] The first step was to collect dilute exhaust in impingers containing aqueous potassium hydroxide, at a rate of 1.02 m^3/hr. The contents of the impingers are acidified and extracted with ethyl ether, and are eventually injected into a gas chromatograph equipped with a flame ionization detector.

Exhaust odor was evaluated using the A.D. Little "Diesel Odorant Analytical System" (DOAS). The procedure used in this study was the same as used in previous studies[5,11], and described in detail in the final report on another study.[12] The vehicle was operated at 3 steady-state modes, idle, 50 kph, and 85 kph. Raw exhaust samples were taken for a specified time so that the required amount of exhaust would pass through the Chromosorb 102 traps. TIA (total intensity of aroma) values are defined by either:

$$TIA = 1 + \log_{10} (LCO, \mu g/\ell)$$

or

$$TIA = 0.4 + 0.7 \log_{10} (LCA, \mu g/\ell),$$

whichever generates the highest value. "LCO" represents liquid column oxygenates, and "LCA" represents liquid column aromatics.

C. Particulate Collection, Mass Rate, and Aerodynamic Sizing

Particulate collection for this project was performed using a 457 mm (18 inch) diameter by 5 m (16 feet) long dilution tunnel operating on total vehicle exhaust. Other associated equipment includes probes, pumps, and filter holders to withdraw and collect the particulate on filters, and a balance to determine the mass of particulate collected.

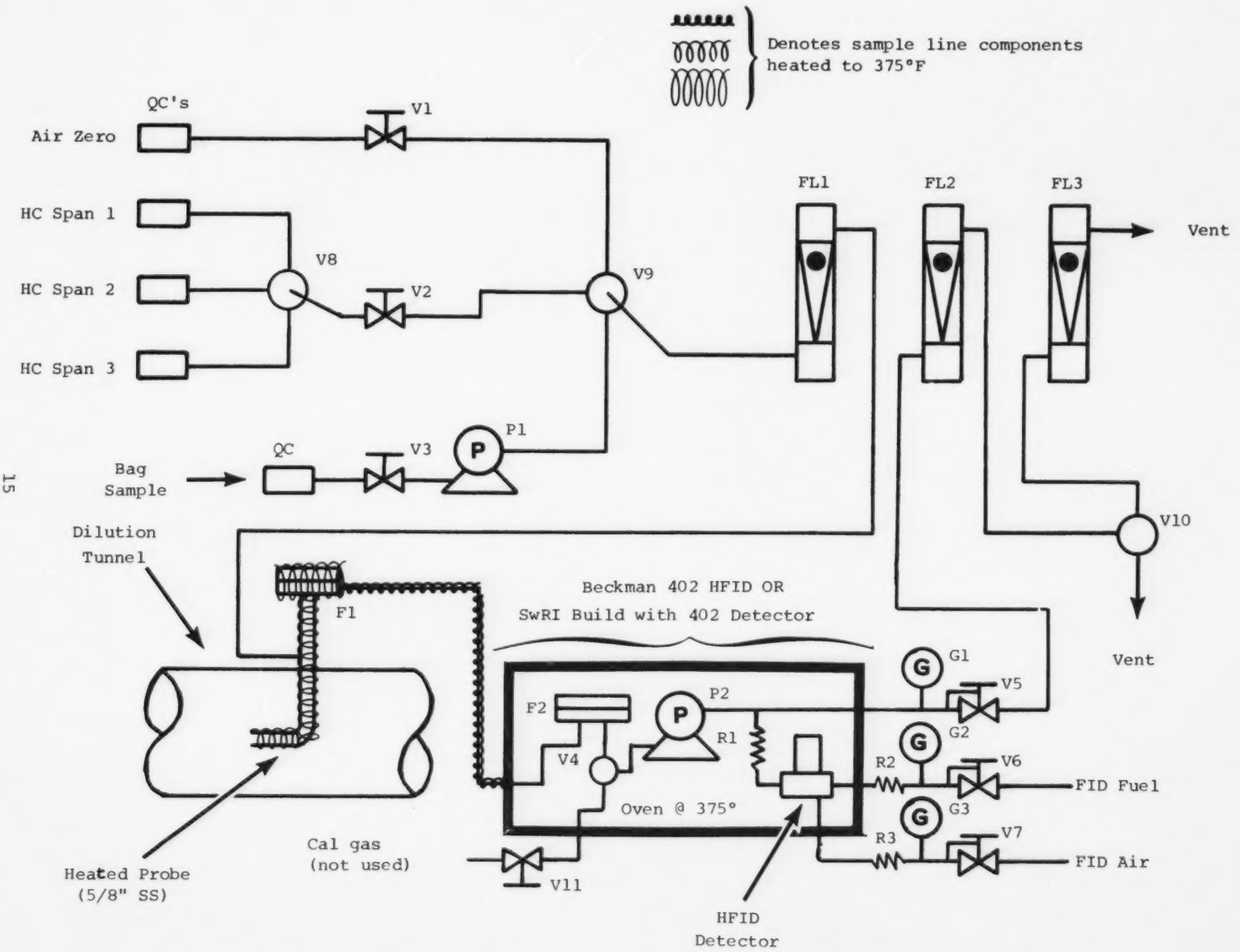

Figure 1. Heated hydrocarbon analyzer system.

TABLE 5. HEATED HYDROCARBON ANALYZER OVERFLOW CALIBRATION AND SAMPLE FLOW SCHEMATIC COMPONENT DESCRIPTION

Component	Designation	Description of Function
Valve	V1	regulating valve for zero air
Valve	V2	regulating valve for HC span gas
Valve	V3	regulating valve for bag sample
Valve	V4	span/zero selector valve in HFID (not used)
Valve	V5	sample backpressure regulator
Valve	V6	FID fuel pressure regulator
Valve	V7	FID air pressure regulator
Valve	V8	HC span selector valve
Valve	V9	HC span/zero/bag sample selector valve
Valve	V10	leak check flow diverter valve
Restrictor	R1	sample capillary
Restrictor	R2	FID fuel restrictor
Restrictor	F3	FID air restrictor
Gage	G1	sample backpressure gage
Gage	G2	FID fuel pressure gage
Gage	G3	FID air pressure gage
Filter	F1	heated 7.0 cm filter (probe)
Filter	F2	heated 7.0 cm filter (oven)
Pump	P1	bag sample pump
Pump	P2	FID heated sample pump
Flowmeter	FL1	overflow flowmeter
Flowmeter	FL2	FID bypass flowmeter
Flowmeter	FL3	leak check flowmeter

The dilution tunnel is similar to that used in a previous study[6], but modified by installing an additional 114 mm (4.5 inch) probe at the downstream end of the tunnel. This large probe was used to withdraw a dilute exhaust sample at a rate of 3.4 m^3/min (120 SCFM) through a 500 x 500 mm (20x20 inch) Pallflex filter (Pall Corporation). The dilution tunnel used is shown schematically in Figure 2. Some of the equipment necessary for collecting particulate and relating it to undiluted vehicle emissions is not shown in the schematic. It includes a constant volume sampler (CVS) operating at a nominal capacity of 12.6 m^3/min (450 CFM) to withdraw and measure unsampled air/exhaust mixture, and the positive-displacement pump (capacity 3.4 m^3/min) used for the 500 x 500 mm filter system. The modified system was used initially in a study[3] just prior to this one, with very satisfactory results.

Figure 3 shows the vehicle in test configuration. The dilution tunnel and filter sampling probes protruding from the tunnel can also be seen in Figure 3. In the foreground, left side, the tunnel exit and the location of the large probe used for the "20x20" system are visible. Figure 4 shows the "20x20" filter holder and the removal of a particulate-laden filter after test. Also visible in Figure 4 is a close-up of the probe system used to withdraw samples through 47 mm filters.

Particle sizing was accomplished using a radial-slot impactor. The impactor system contained stainless steel stages on which particulate matter was supposedly fractionated by size, and a final Pallflex backup filter. The impactor was located at the downstream end of the dilution tunnel. Figure 5 shows the impactor system disassembled with the stages, plates, and filter removed from their holder for clarity. In operation, each stage was placed on a plate such that the slots in each stage decreased in width from sample entrance down to the filter. Each stage was rotated 45 degrees so the particulate matter passing through the slots impacted on a solid portion of the following plate. Particle retention characteristics were related to the slot size and flowrate through the impactor. The flowrate was controlled using a metal bellows vacuum pump, pressure gauge, and flowmeter. The flowrate was maintained at 2.8 ℓ/min (0.1 CFM) to achieve particle sizing down to 0.1 micron.

The mass of particulate matter collected on sample filters and impactor discs was determined on a microbalance. This balance is enclosed in a vibration-resistant, temperature- and humidity-controlled chamber to minimize outside interferences. Filters and other materials for weighing were allowed to stabilize in the chamber for a minimum of 12 hours before they were weighed. The sensitivity of the balance is 1 μg. Air to the chamber flows at about 17 m^3/hr on a one-pass basis, and keeps the chamber pressure at about 2.5 kPa above atmospheric. The control system keeps chamber conditions at 22.2 ± 0.6°C and 63 ± 2 percent relative humidity, and air entering the chamber is filtered through a 99.99 percent DOP-efficient filter. Figure 6 shows a technician weighing a 47 mm filter after test, using the weighing chamber.

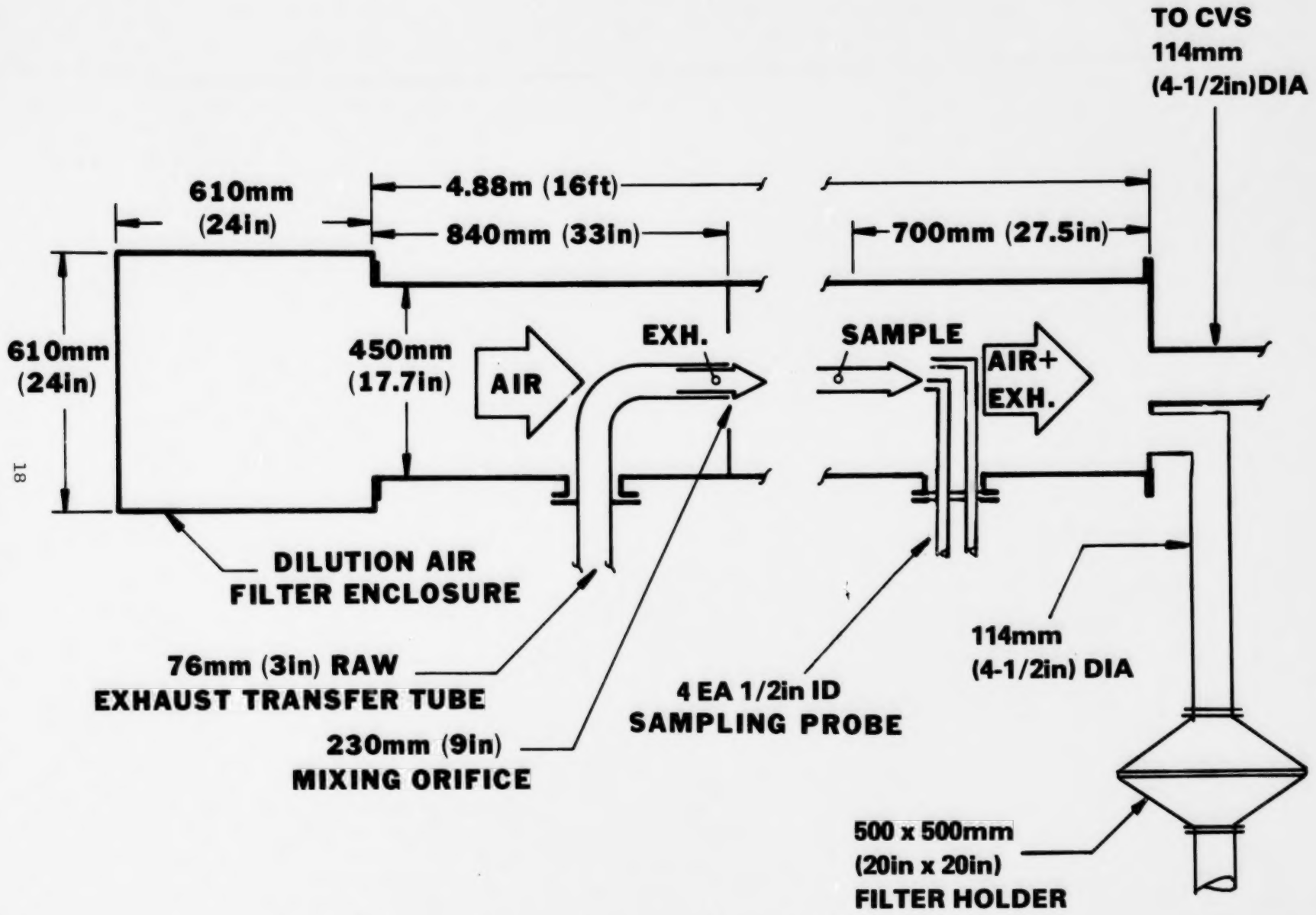

Figure 2. Schematic diagram of exhaust dilution tunnel.

Figure 3. Volkswagen Rabbit during test.

Figure 4. Unloading of 20x20 filter from holder.

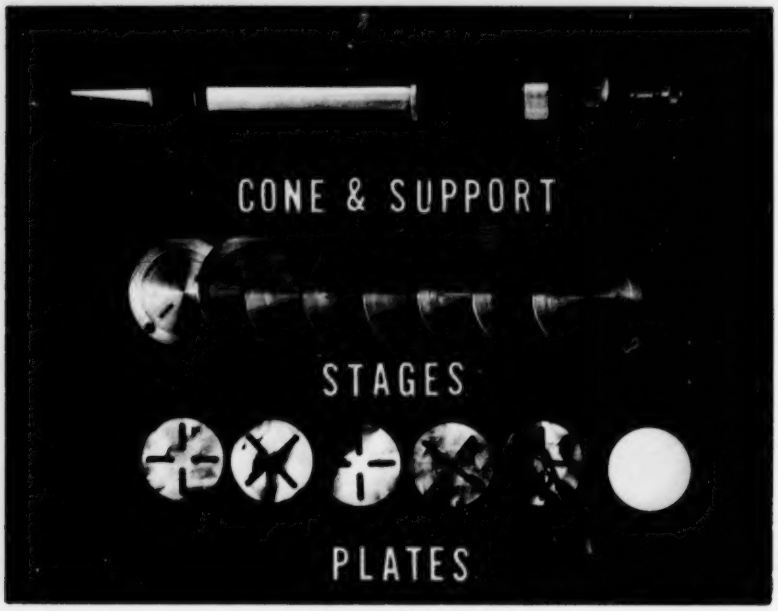

Figure 5. Particle sizing impactor, disassembled.

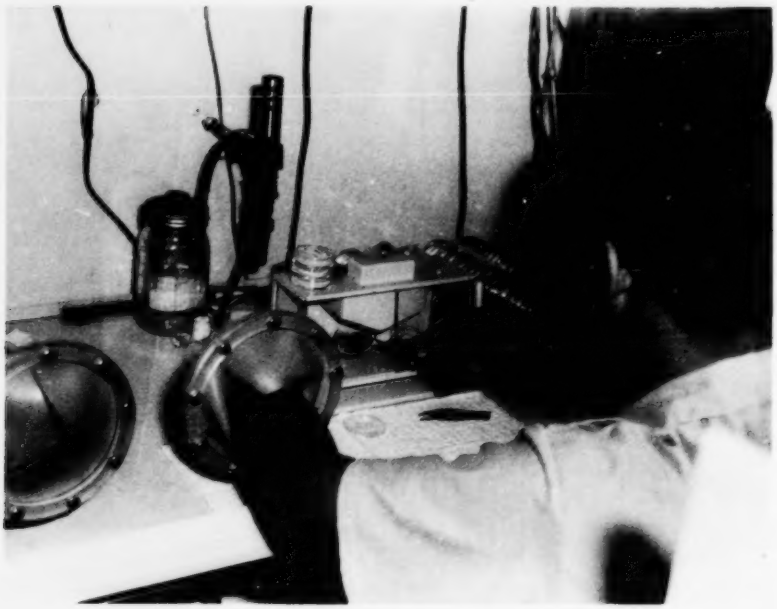

Figure 6. Filter weighing in a temperature- and humidity-controlled chamber.

D. Analysis of Particulate Composition

Particulate samples were acquired by several methods for various analyses. After determining particulate matter weights, the samples were subjected to analysis for major elements and trace elements. Some particulate samples were collected in order to obtain the soluble fraction of particulate matter. Analysis of the soluble fraction is discussed in the next section.

1. Trace Elements

Analysis for trace elements (metals and sulfur) in the particulate matter was performed on 47 mm Fluoropore filter samples. As provided in the contract agreement, these determinations were made at EPA's Research Triangle Park laboratories as part of the EPA in-house measurement program. The instrumentation used for these analyses was a Siemens MRS-3 x-ray fluorescence spectrometer.

2. Major Elements

Samples collected on 47 mm glass fiber filters were sent to Galbraith Laboratories and analyzed for carbon and hydrogen content by combustion and subsequent gas analysis. The equipment used was a Perkin-Elmer Model 240B automated thermal conductivity CHN analyzer. Results of this analysis was reported in percent of submitted mass and weight of element detected on the filter. These results make the filter weighing accuracy very important.

E. Analysis of the Soluble Fraction of Particulate Matter

The soluble fraction of particulate matter was obtained by extraction from the 500 x 500 mm (20x20 inch) Pallflex filters. This large filter enabled enough soluble material to be extracted so that the total amount could be divided into smaller aliquots, then analyzed for a variety of constituents.

1. Total Soluble Organics

The 500 x 500 mm filters were weighed before and after test to determine the weight of particulate matter. Each filter was extracted using methylene chloride in a Soxhlet apparatus. The solvent volume was reduced at low temperature and under vacuum. The remaining solvent/solubles were transferred to a preweighed container, and the solvent was evaporated by nitrogen purging. The total mass of solubles was determined gravimetrically, and the percent of solubles in the particulate matter calculated.

2. Major Elements

One aliquot of the dried, weighed soluble extract was submitted to Galbraith Laboratories and analyzed for carbon, hydrogen, oxygen, and sulfur

by the technique and instrumentation described in Section IV, D.2 (Perkin-Elmer 240B). An additional aliquot of soluble extract was submitted to SwRI's Mobile Energy Division for nitrogen analysis by oxidative pyrolysis and chemiluminescence.

3. Solubles Boiling Range and Individual n-Paraffin Analysis

Another aliquot of soluble extract was submitted to SwRI's Mobile Energy Division for determination of the boiling range and reference to normal paraffins. The procedure is a high-temperature variation of ASTM D2887-73. Each aliquot was dissolved in carbon disulfide, and an internal standard (C_9 and C_{11} compound) was added for quantitative results. The maximum temperature that this column reached was 450°C, eluting compounds boiling up to 650°C.

4. Benzo(a)pyrene (BaP) and Ames Bioassay

An additional 500 x 500 mm (20x20 inch) filter was extracted, and the extract was divided into eleven aliquots. One aliquot was used to determine the BaP content of the soluble extract. This analysis was performed by SwRI's Department of Emissions Research. The procedure, developed by others[13], is based on high-performance liquid chromatography to separate BaP from other organic solubles in particulate matter; and it incorporated fluorescence detection to measure BaP. The instrument used was a Perkin-Elmer 3B liquid chromatograph equipped with a MPF-44 fluorescence spectrophotometer. Excitation was at a wavelength of 383 nm, and emission was read at 430 nm. The remaining ten aliquots were shipped on dry ice to EG&G for Ames bioassay testing. The Ames test refers to a bacterial mutagenesis plate assay with Salmonella typhimurium, according to the method of Ames.[14]

5. Fractionation by Relative Polarity

The composition of the organic soluble portion of the particulate matter is complex, and its separation into individual compounds is very difficult. Fractionation of the solubles by high performance liquid chromatography (HPLC) separates the sample into a series of fractions of increasing molecular polarity. This procedure is discussed in detail in a CRC report.[15] Briefly, an organic solubles sample is initially carried in a solvent composed of 95 percent hexane and 5 percent methylene chloride, a relatively non-polar mixture. After a period of time, the ratio of methylene chloride to hexane, and therefore solvent polarity, is increased at a rate of 5 percent methylene chloride per minute. At 100 percent methylene chloride, the carrier solvent is moderately polar. A fluorescence detector is used at an excitation wavelength of 303 nm and an emission wavelength of 418 nm. A UV detector is used at wavelength of 254 nm. At these wavelengths fluorescence and UV responses of compounds are mapped as a function of column elution time, reflecting polarity.

V. TEST PLANS AND OPERATING SCHEDULE

The following sections describe the test plan, sequences, and schedule. A summary of the exhaust constituents evaluated is summarized in Table 6. Test efficiency was achieved by grouping similar sample collection techniques together, to minimize vehicle running time. Discussion of the analysis techniques are presented in Section IV of this report.

The vehicle followed two transient cycles, FTP and HFET, during most sample collection and measurement runs. These cycles are routinely used in emission testing and are well documented in other works.[1,3,6,11] Smoke evaluation was performed separately during the cold transient portion of the FTP (first 505 seconds). The cold transient portion incorporates all of the most interesting modes from a smoke standpoint, including cold engine start, first idle, first acceleration, second idle, and second acceleration. Steady-state modes at idle, 50 kph, and 85 kph were used to obtain raw exhaust samples for odor analysis. Vehicle running time on the steady-state modes was governed by the sample volume requirements of the odor measurement procedure (DOAS).

The test plan incorporating the cycles and evaluations for each test fuel is given in Table 7. Samples taken over each 2-bag FTP were defined as a "cold FTP" or a "hot FTP." Testing for each fuel required a minimum of three days. After the first day of testing, as many of the results as possible were reviewed to determine whether or not replicate analysis would be required on the second day of testing. It was important to determine the validity of the tests as early as possible, to avoid costly reruns and depletion of limited test fuel quantities by repurging the fuel system. Procedure for fuel system purging between test fuels is discussed in Section IV. Duplicate filter samples were collected on Day 2, and retained for possible replicate analyses. In some cases, samples were stored in their most stable form, then submitted for analysis as a group (rather than individually) to minimize the effects of day-to-day variability in an analytical procedure.

Utilizing this test plan on nine test fuels yielded a total of 30 runs, including baseline repeats and additional runs to support unexpected results. At the Project Officer's request, several initial tests were performed to determine lab-to-lab correlation of test results on the vehicle. Also, some testing was requested to determine whether or not the vehicle used in the study could be run to simulate an earlier model used in another study. These efforts are discussed in Section III, Part A.

TABLE 6. OUTLINE OF CHEMICAL AND PHYSICAL EXHAUST EVALUATIONS

Exhaust component under study	Constituent(s) analyzed for	Collection Method	Analysis technique(s)
Smoke	smoke (visible)	---	EPA smokemeter (continuous)
gases	HC, CO, CO_2, NO_x	sample bag	constant volume sampler
	aldehydes	wet impinger	DNPH
	odor	DOAS traps	DOAS analyzer
	phenols	wet impinger	extraction, GC
particulate	total mass	Pallflex filters	gravimetric
	size distribution	impactor-filter	gravimetric
	sulfur & trace elements	filter, 47 mm Fluoropore	x-ray fluorescence
	carbon, hydrogen in particulate	filter, 47 mm glass fiber	combustion (commercial)
	organic extractable substances	"20x20" filter	soxhlet extraction
	BaP in organic solubles	---	LC, fluorescence detection
	molecular weight range of organic solubles	---	GC
	carbon, hydrogen in solubles	---	combustion (commercial)
	biological response of solubles	---	Ames bioassay
	polarity profile of solubles	---	HPLC

TABLE 7. TEST PLAN FOR EACH FUEL

Analysis or Sample	Day 1			Day 2[a]						Day 3 cold transient (505 seconds)
	Cold FTP	Hot FTP	HFET	Idle	50 kph	85 kph	Cold FTP	Hot FTP	HFET	
gaseous HC, CO, NO_x, CO_2	X	X	X	X	X	X	X	X	X	-
sulfur & trace metals	X	X	X	-	-	-	-	-	-	-
particle size distribution	—X[b]—			-	-	-	-	-	-	-
organic extractables[c]	X	X	X	-	-	-	-	-	-	-
total particulate mass	X	X	X	X	X	X	X	X	X	-
C & H in particulate	X	X	X	-	-	-	-	-	-	-
odor	-	-	-	X	X	X	X	X	-	-
aldehydes	-	-	-	-	-	-	X	X	X	-
phenols	-	-	-	-	-	-	X	X	X	-
BaP and Ames bioassay	-	-	-	-	-	-	X	X	X	-
smoke	-	-	-	-	-	-	-	-	-	X

[a] Repeat samples optional
[b] One sample collected for entire 4-bag FTP
[c] Organic extractables divided into aliquots for HPLC, carbon & yydrogen, and boiling range analyses

VI. GASEOUS EMISSION AND ODOR RESULTS

This report section includes presentation and discussion of results on regulated gaseous emissions, aldehydes, phenols, and exhaust odor. Data on regulated gaseous emissions, including CO_2 and fuel consumption, were obtained by analysis of bag samples collected from the CVS-diluted exhaust. In most cases, confidence limits could not be calculated due to an insufficient number of data points. For a few emissions, sufficient replicate tests were performed on base fuel only to allow computation of confidence limits. Where applicable, these limits are shown as the standard error bar on the graphical presentations. Emissions repeatability was good in most cases, with replicate results on the same fuel deviating 5 percent or less from results of the first run. When emissions differed by more than about 5 percent between runs on different fuels, the emissions variation was considered likely to be a result of fuel property variation.

A. Regulated Gaseous Emission Results

Data on regulated gaseous emissions, including CO_2 and fuel consumption, were obtained by analysis of bag samples collected from the CVS-diluted exhaust. These results are summarized in Tables 8 and 9. The results are reported for each individual bag, a calculated 3-bag FTP, and a calculated 4-bag FTP. The computer printouts for each test are located in Appendix C, pages C-2 through C-71.

Vehicle performance using fuel blend EM-475-F, base fuel and 35 percent SRC-II, was marginal. A complete FTP was not possible due to the high level of emissions, causing sample system plugging. The only results obtainable were for the first 505 seconds of a cold-start FTP. The gaseous emissions, as shown in Table 7, indicate significant increases in HC, CO, NO_x, and fuel consumption. Probable cause for these increases was the inability of the engine to produce normal power at normal rack settings on this low cetane number (31) fuel. Use of EM-475-F required more rack opening to operate the vehicle over the FTP driving schedule. This increase in rack position, and consequent larger volume of fuel injected, is confirmed by the increase in fuel consumption noted. With overall richer off-design engine operation, an increase in emissions was expected.

The "3-bag" composite values for HC, CO, NO_x from Table 8 are shown as a bar graph in Figure 7. The greatest hydrocarbon and carbon monoxide increases, as compared to the base fuel, were observed with the Broadcut and the 25% SRC-II blend. Hydrocarbon emissions with these two fuels more than doubled as compared to the base fuel. An earlier study[6], using a similar vehicle operating on various petroleum-based fuels, reported increases in HC

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TABLE 8. AVERAGE REGULATED GASEOUS EMISSIONS DATA DURING FTP

Fuel	Item	Emissions (g/km) and Fuel Usage (ℓ/100 km)					
		FTP Bag Number				3-bag FTP[a]	4-bag FTP[a]
		1	2	3	4		
Base DF-2 EM-329-F	HC	0.40	0.26	0.33	0.25	0.31	0.31
	CO	1.23	0.82	1.03	0.80	0.96	0.95
	CO_2	179.	164.	156.	163.	165.	165.
	NO_x	0.67	0.67	0.64	0.66	0.66	0.66
	Fuel	6.94	6.33	5.95	6.32	6.37	6.36
Shale Diesel Fuel-Marine EM-453-F	HC	0.42	0.26	0.34	0.27	0.31	0.32
	CO	1.33	0.88	1.17	0.84	1.06	1.04
	CO_2	187.	167.	163.	164.	171.	170.
	NO_x	0.68	0.67	0.67	0.68	0.67	0.68
	Fuel	7.31	6.49	6.37	6.37	6.63	6.59
Paraho JP-5 EM-473-F	HC	0.48	0.28	0.49	0.29	0.38	0.38
	CO	1.41	1.04	1.33	1.00	1.20	1.19
	CO_2	182.	163.	156.	158.	165.	165.
	NO_x	0.71	0.69	0.68	0.69	0.70	0.69
	Fuel	7.30	6.53	6.30	6.32	6.62	6.56
Coal Case 5A EM-474-F	HC	0.51	0.30	0.46	0.32	0.39	0.39
	CO	1.49	1.00	1.39	1.03	1.21	1.22
	CO_2	187.	166.	160.	157.	169.	166.
	NO_x	0.84	0.85	0.79	0.83	0.83	0.82
	Fuel	6.92	6.11	5.94	5.78	6.23	6.13
Broadcut EM-476-F	HC	1.04	0.55	0.65	0.61	0.68	0.70
	CO	1.58	1.35	1.27	1.36	1.38	1.38
	CO_2	181.	162.	158.	157.	164.	163.
	NO_x	0.65	0.67	0.60	0.64	0.65	0.64
	Fuel	7.36	6.51	6.36	6.34	6.64	6.59
35% SRC-II EM-475-F	HC	3.52	--	--	--	--	--
	CO	3.05	--	--	--	--	--
	CO_2	222.6	--	--	--	--	--
	NO_x	0.98	--	--	--	--	--
	Fuel	8.52	--	--	--	--	--
25% SRC-II EM-478-F	HC	1.18	0.47	0.41	0.42	0.60	0.59
	CO	1.48	1.29	1.22	1.26	1.31	1.30
	CO_2	191.	171.	163.	159.	173.	170.
	NO_x	0.78	0.76	0.73	0.75	0.76	0.7
	Fuel	7.17	6.36	6.08	5.93	6.45	6.33
25% EDS EM-482-F	HC	0.48	0.26	0.35	0.25	0.33	0.32
	CO	1.50	0.94	1.26	0.95	1.14	1.14
	CO_2	181.3	159.9	154.6	153.6	162.8	161.0
	NO_x	0.72	0.74	0.71	0.73	0.73	0.73
	Fuel	6.83	5.98	5.81	5.74	6.11	6.04
25% EDS Naphtha EM-485-F	HC	0.41	0.29	0.39	0.25	0.34	0.33
	CO	1.37	1.05	1.23	0.96	1.16	1.14
	CO_2	190.9	167.8	160.4	159.8	170.6	168.2
	NO_x	0.76	0.78	0.71	0.75	0.76	0.75
	Fuel	7.38	6.47	6.21	6.15	6.59	6.49

[a]Calculated

TABLE 9. AVERAGE RESULTED GASEOUS EMISSIONS DATA DURING HFET AND STEADY-STATE

Fuel	Item	Emissions (g/km) and Fuel Usage (ℓ/100 km)			
			Steady-State		
		HFET	Idle[a]	50 kph	85 kph
Base DF-2 EM-329-F	HC	0.35	2.13	0.17	0.39
	CO	1.04	9.30	0.54	1.20
	CO_2	133.	1136.	126.	134.
	NO_x	0.61	5.78	0.53	0.67
	Fuel	5.17	0.44	4.77	5.22
Shale Diesel Fuel-Marine EM-453-F	HC	0.37	2.94	0.24	0.40
	CO	1.20	9.45	0.70	1.35
	CO_2	146.	1169.	123.	142.
	NO_x	0.67	6.09	0.54	0.69
	Fuel	5.66	0.45	4.73	5.49
Paraho JP-5 EM-473-F	HC	0.79	2.10	0.09	0.61
	CO	1.60	11.3	0.39	1.81
	CO_2	139.	1067.	107.	142.
	NO_x	0.66	6.90	0.51	0.72
	Fuel	5.71	0.43	4.25	5.79
Coal Case 5A EM-474-F	HC	0.46	7.23	0.45	0.63
	CO	1.41	22.1	0.51	1.79
	CO_2	145.	1176.	108.	148.
	NO_x	0.84	6.18	0.42	0.92
	Fuel	5.38	0.45	3.99	5.55
Broadcut EM-476-F	HC	0.61	11.0	0.20	0.71
	CO	1.18	24.5	0.47	1.29
	CO_2	138.	1117.	106.	135.
	NO_x	0.58	5.67	0.41	0.61
	Fuel	5.57	0.47	4.21	5.49
35% SRC-II EM-475-F	HC	--	--	--	--
	CO	--	--	--	--
	CO_2	--	--	--	--
	NO_x	--	--	--	--
	Fuel	--	--	--	--
25% SRC-II EM-478-F	HC	0.28	11.6	0.64	0.25
	CO	0.92	26.4	0.56	0.83
	CO_2	142.	1097.	118.	144.
	NO_x	0.76	0.75	0.45	0.84
	Fuel	5.25	0.43	4.39	5.34
25% EDS EM-482-F	HC	0.34	6.60	0.17	0.31
	CO	1.12	18.09	0.37	1.11
	CO_2	136.1	1097.	103.0	136.5
	NO_x	0.71	5.79	0.43	0.82
	Fuel	5.12	0.42	3.84	5.13
25% EDS Naphtha EM-485-F	HC	--	--	--	--
	CO	--	--	--	--
	CO_2	--	--	--	--
	NO_x	--	--	--	--
	Fuel	--	--	--	--

[a]Emission in g/h instead of g/km, fuel in ℓ/h instead of ℓ/100 km

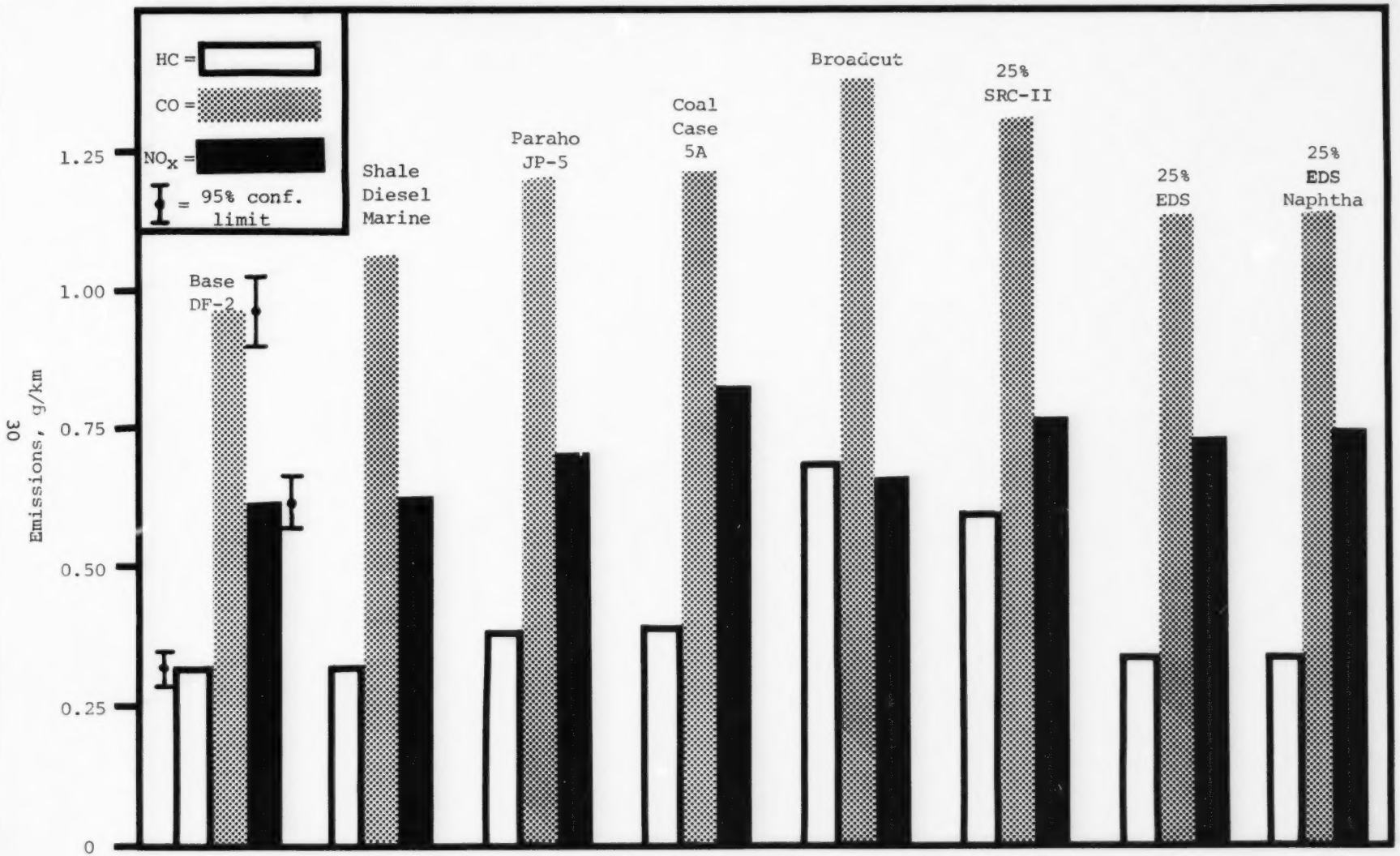

Figure 7. Regulated gaseous emissions during FTP (composite)

and CO emissions of up to 4 times the base fuel level. The cetane numbers of the two fuels in that study were 49 and 42. The cetane number spread between the fuels in this study was greater (50 to 35 and 38), but smaller HC increases were noted. Probable cause for the Broadcut fuel's low cetane number was the presence of low molecular weight paraffins, while the 25% SRC-II fuel's low cetane was probably attributable to its rather high aromatic content.

All the test fuels resulted in higher NO_x emissions than the base fuel. Use of the Coal Case 5A material resulted in higher NO_x emissions than the other blends. Another study[3] resulted in developing prediction equations for several emissions as a function of fuel properties. NO_x emissions were associated with fuel aromatic and nitrogen content. The Coal Case 5A fuel contained high aromatics and nitrogen. The prediction equations themselves could not be used per se, as they contain a constant term which is applicable to the specific vehicle/engine tested (Mercedes-Benz 240D). A similar statistical analysis incorporating the wide variance in fuel properties of this study could yield similar prediction equations. Comparing the two middle-distillate coal-derived fuel blends, 25% SRC-II and 25% EDS, the SRC-II blend was associated with high emissions. The 25% middle-distillate and the 25% EDS naphtha gave almost identical HC, CO and NO_x emissions.

Figure 8 shows HFET results in bar graph form similar to Figure 7. The 25% EDS naphtha was not run on the HFET. It was only used on a limited basis for very few tests. Complete evaluation of the 25% EDS naphtha may occur in another study if preliminary results generated during this study are of sufficient interest. Paraho JP-5 was associated with more substantial HC and CO increases on the HFET, as compared with the base fuel, than was the case for the FTP. Coal Case 5A increased HFET NO_x over baseline more than the other blends, and it also increased CO about 40 percent. It is interesting to note that the 25% EDS blend gave slightly higher HC and CO (NO_x about the same) as compared with the 25% SRC-II. Similar comparison between these two blends during the FTP indicated the opposite trend.

Fuel consumptions for the test fuels during both transient cycles are shown graphically in Figure 9. During both cycles, all the test blends showed slightly increased fuel consumption except Coal Case 5A and 25% EDS. The 25% EDS appears to result in the same or slightly lower fuel consumption as compared with the base fuel. Coal Case 5A showed increased fuel consumption over the base fuel during the HFET, but was about the same during the FTP. FTP and HFET results indicate that the 25% EDS blend was associated with between 5 (FTP) and 12 (HFET) percent less fuel consumed as compared with the 25% SRC-II blend.

B. Aldehyde and Phenol Results

Concentrations of a number of individual low-molecular weight aldehydes were determined in CVS-diluted exhaust. The results for each aldehyde species

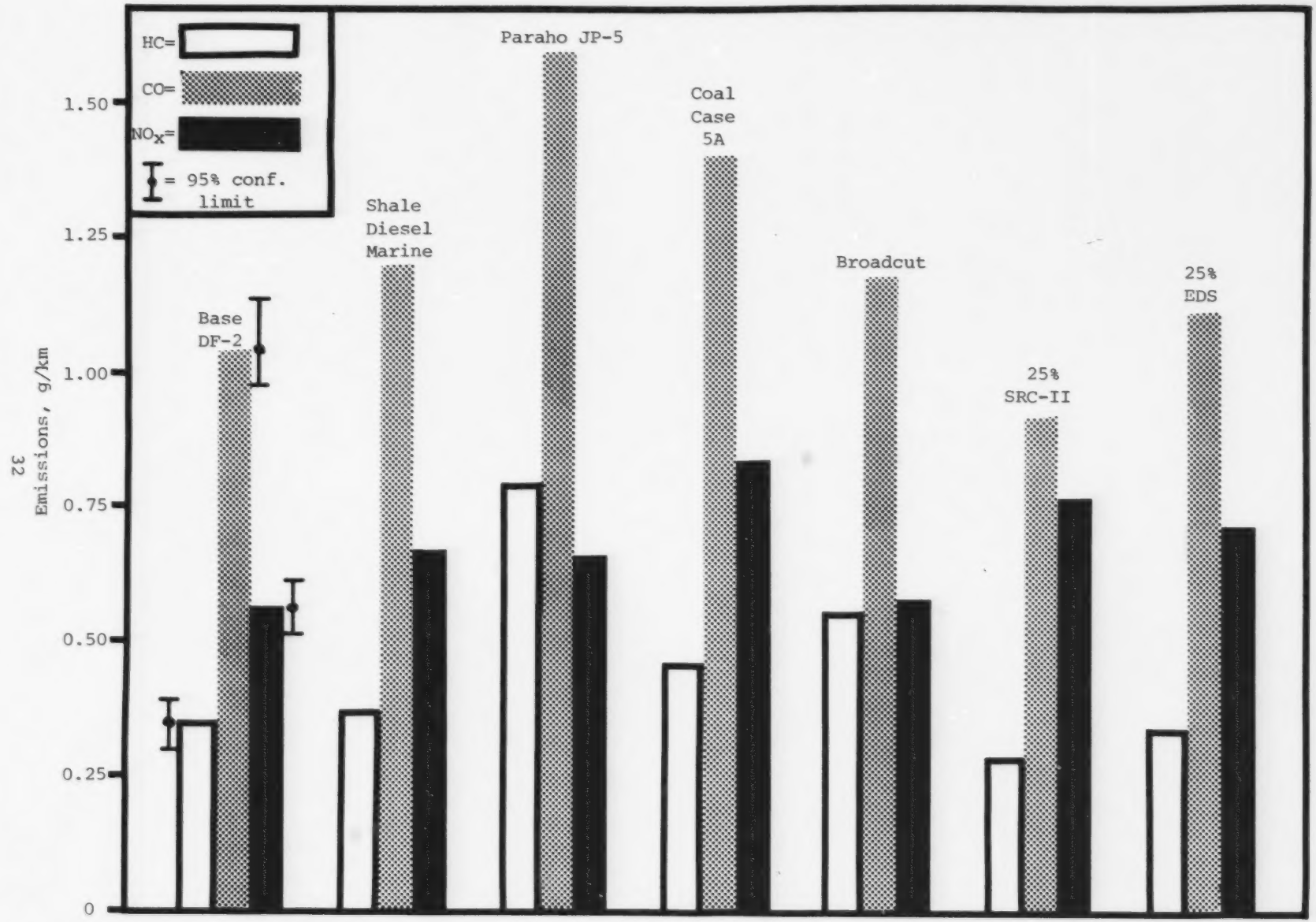

Figure 8. Regulated gaseous emissions during HFET.

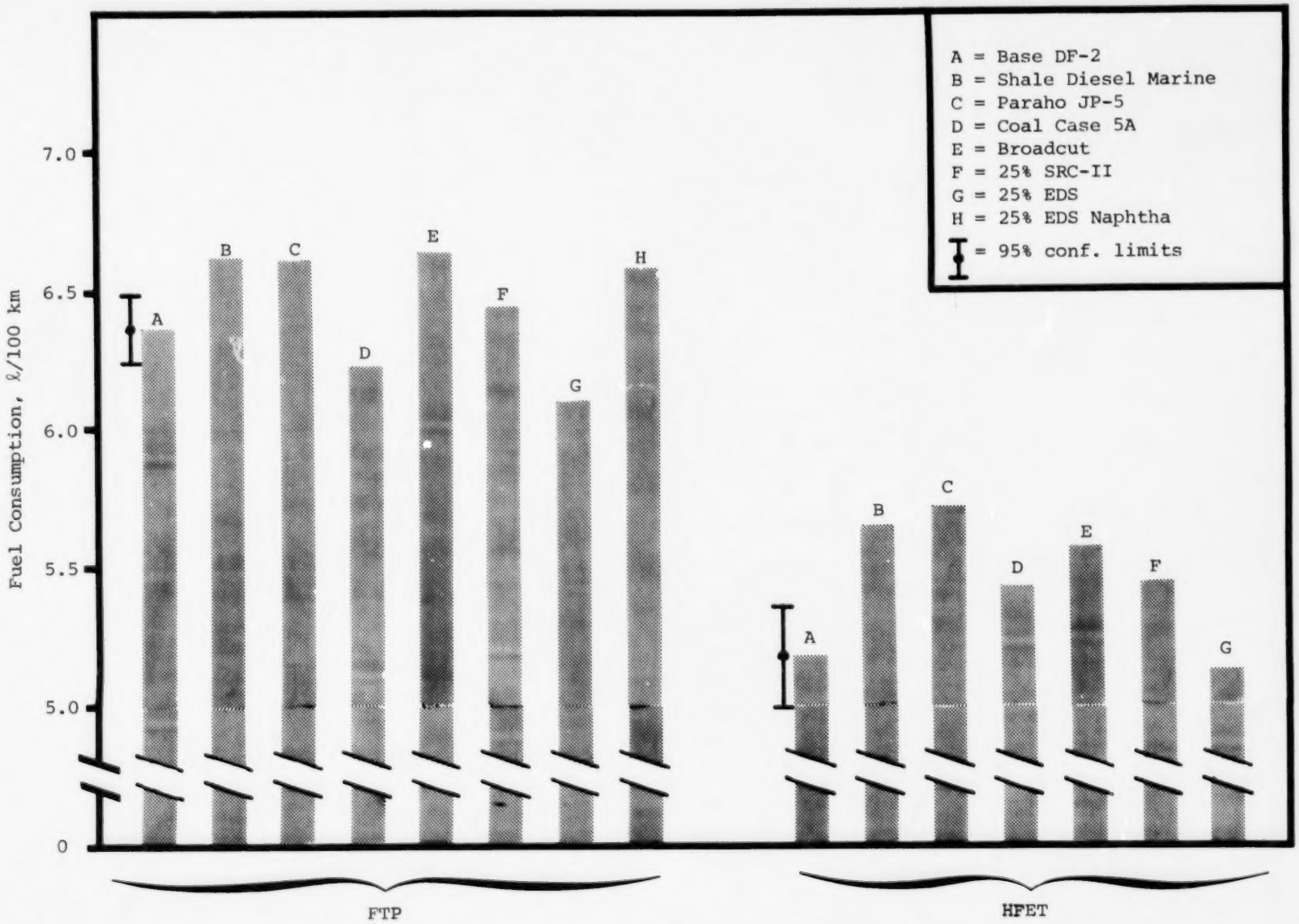

Figure 9. Fuel consumption during FTP and HFET

and their sums during the FTP are presented in Table 10. "Total" aldehydes refers to the sum of the aldehydes determined using the procedure discussed in Section IV. This "total" for each of the test fuels is shown graphically in Figure 10. Table 11 contains the phenol results during the FTP and the "total" phenols are also shown graphically in Figure 10.

"Total" aldehyde emission decreases, as compared with the base, were observed with the 25% SRC-II and the 25% EDS blends. Both blends gave similar aldehyde emissions (≈3 mg/km). No aldehyde increases over the base were seen with the fuels tested during the FTP. Paraho JP-5 and Broadcut test fuel were associated with decreases in FTP phenol emissions as compared to base fuel. The 25% EDS blend doubled the base fuel's phenol emissions during the FTP. It is interesting to note that although the aldehyde emission rates for the 25% SRC-II and 25% EDS blend were approximately the same, the 25% SRC-II blend did not increase phenols as did the 25% EDS blend.

Aldehyde and phenol results during the HFET are listed in Table 12. Their "total" values are shown as a bar graph in Figure 11. As seen in the FTP results, no "total" aldehyde increases were observed when compared to the base fuel's results. Again, aldehyde decreases were seen with the 25% SRC-II and 25% EDS blends. Phenol decreases during the HFET were associated with the Paraho JP-5 and the Broadcut test blend (same trend as FTP). The 25% SRC-II blend, however, increased phenols to over 14 times the base fuel level during the HFET. The same blend did not affect phenols during the FTP. A similar situation occurred with the 25% EDS phenol results. No change was observed during the HFET, but an increase was seen during the FTP. Coal Case 5A more than doubled the base fuel's phenol emissions during the HFET.

C. Results of Odor Analysis

This subsection contains results from instrumental odor evaluations (DOAS). The chromatographic procedure separates an oxygenate fraction (liquid column oxygenates, LCO) and an aromatic fraction (liquid column aromatics, LCA). Studies[12,16] have been made in an attempt to correlate instrumental analysis to a panel of trained human evaluators. One study[16] indicated that TIA (LCO-based) of less than 1.0 would be rated by a trained panel at less than "D"-1. A perceived odor intensity of "D"-1 by the Turk method is considered a light (barely perceptible) odor. It should be noted that since the TIA (total intensity of aroma) is calculated using a logarithmic equation, each increase of one unit in the TIA value relates to a concentration increase by a factor of ten.

Results of the odor analysis are listed in Table 13. The TIA values (LCO-based) are shown graphically in Figure 12. During idle operation, the Broadcut and 25% SRC-II blends increased odor as compared to the base. A slight reduction was observed with the Paraho JP-5. At the 50 kph cruise condition, the Coal Case 5A was associated with the highest odor levels as

TABLE 10. FTP ALDEHYDE EMISSIONS DATA

Operating Schedule	Compound(s) mg/km	Fuel Description and Code (EM-XXX-F)						
		Base DF-2 329	Shale Diesel Marine 453	Paraho JP-5 473	Coal Case 5A 474	Broad-cut 476	25% SRC-II 478	25% EDS 482
Cold FTP	Formaldehyde	7.	7.	8.	4.	14.	3.	5.
	Acetaldehyde	2.	1.	2.	0.0	0.7	0.0	0.0
	Acetone[a]	2.	0.0	0.0	0.0	0.0	0.0	0.0
	Hexanaldehyde	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Benzaldehyde	0.0	2.	8.	0.0	3.	0.0	0.0
	"Total"	11.	10.	18.	4.	18.	3.	5.
Hot FTP	Formaldehyde	10.	6.	6.	7.	6.	2.	0.0
	Acetaldehyde	2.	1.	3.	3.	0.0	0.0	0.0
	Acetone[a]	3.	0.0	0.0	0.0	0.0	0.0	0.2
	Hexanaldehyde	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Benzaldehyde	0.0	2.	0.0	0.0	3.	0.0	1.
	"Total"	15.	9.	9.	10.	9.	2.	1.
Calculated 1981 FTP	Formaldehyde	9.	6.	7.	6.	9.	2.	2.
	Acetaldehyde	2.	1.	3.	2.	0.0	0.0	0.0
	Acetone[a]	3.	0.0	0.0	0.0	0.0	0.0	0.1
	Hexanaldehyde	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Benzaldehyde	0.0	2.	3.	0.0	3.	0.0	0.6
	"Total"	14.	9.	13.	8.	12.	2.	3.

[a]Included acrolein and propanol

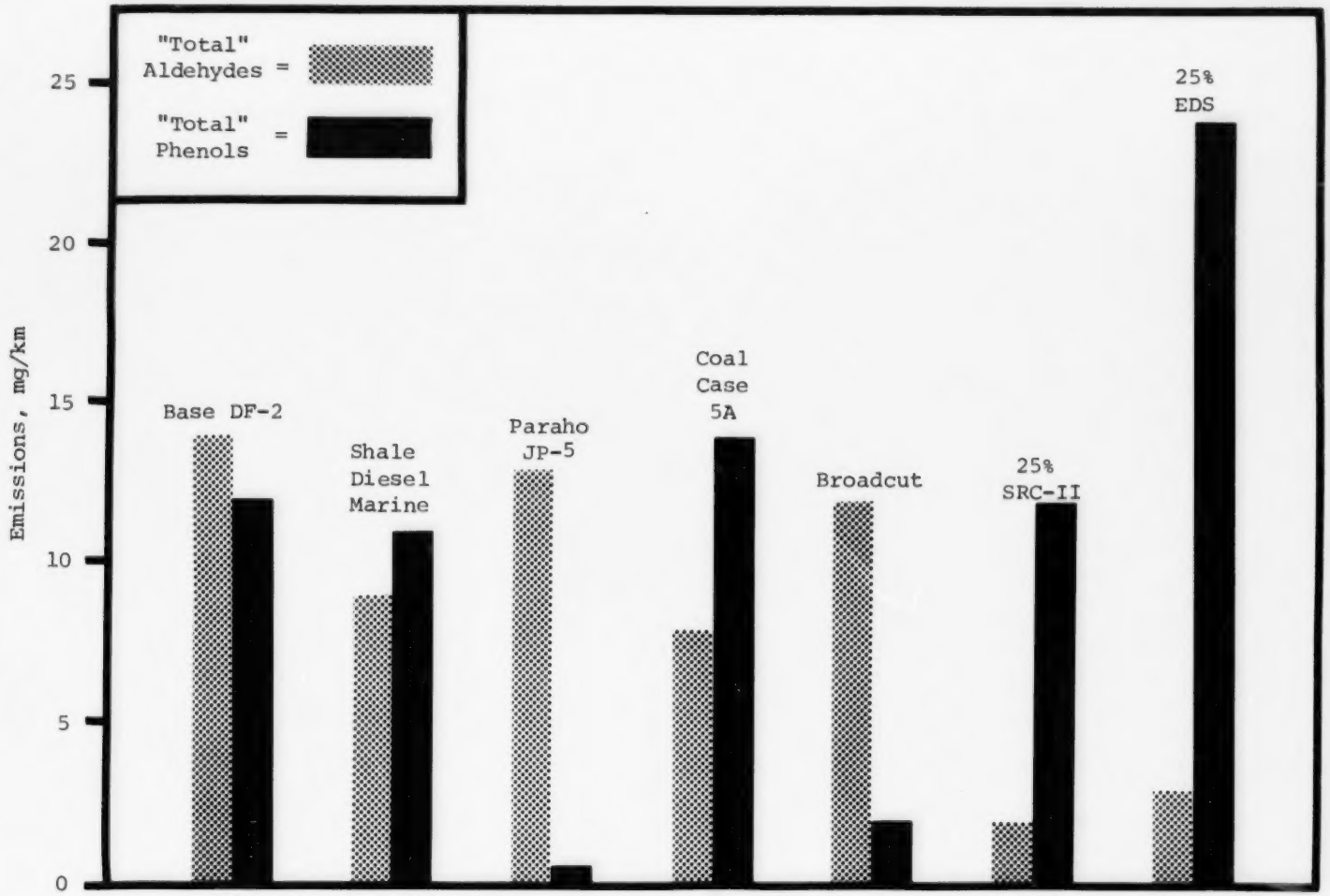

Figure 10. "Total" aldehyde and phenol emissions during FTP.

TABLE 11. FTP PHENOL EMISSIONS DATA

Operating Schedule	Compound(s) mg/km	Fuel Description and Code (EM-XXX-F)						
		Base DF-2 329	Shale Diesel Marine 453	Paraho JP-5 473	Coal Case 5A 474	Broad-cut 476	25% SRC-II 478	25% EDS 482
Cold FTP	Phenol	0.0	0.0	0.0	0.0	0.0	0.0	0.9
	Salicylaldehyde	0.0	0.0	0.0	0.0	0.0	3.	1.
	m-Cresol + p-Cresol	1.	3.	0.0	0.0	0.5	1.	1.
	Group 5[a]	4.	0.0	0.0	0.5	0.0	0.2	1.
	2,3,5-trimethylphenol	0.4	0.0	0.0	0.0	0.0	0.4	0.6
	2,3,5,6-tetramethylphenol	0.3	0.0	0.5	0.0	5.	14.	5.
	2-n-propylphenol	7.	8.	0.0	16.	0.0	0.0	0.0
	"Total"	13.	11.	0.5	17.	6.	19.	10.
Hot FTP	Phenol	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Salicylaldehyde	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	m-Cresol + p-Cresol	0.1	0.6	0.0	2.4	0.0	0.5	0.4
	Group 5[a]	2.	0.0	0.0	0.0	0.0	0.0	0.4
	2,3,5-trimethylphenol	0.1	0.0	0.0	0.0	0.0	0.0	0.6
	2,3,5,6-tetramethylphenol	0.2	0.0	0.5	0.0	0.0	7.	33.
	2-n-propylphenol	8.	10.	0.0	9.8	0.0	0.0	0.0
	"Total"	10.	11.	0.5	12.	0.0	8.	34.
Calculated 1981 FTP	Phenol	0.0	0.0	0.0	0.0	0.0	0.0	0.4
	Salicylaldehyde	0.0	0.0	0.0	0.0	0.0	1.	0.4
	m-Cresol + p-Cresol	0.7	2.	0.0	1.4	0.2	1.	0.7
	Group 5[a]	3.	0.0	0.0	0.2	0.0	0.1	0.7
	2,3,5-trimethylphenol	0.3	0.0	0.0	0.0	0.0	0.2	0.6
	2,3,5,6-tetramethylphenol	0.3	0.0	0.5	0.0	2.	10.	21.
	2-n-propylphenol	8.	9.	0.0	12.5	0.0	0.0	0.0
	"Total"	12.	11.	0.5	14.	2.	12.	24.

[a]Group 5 consists of p-ethylphenol, 2-isopropylphenol, 2,3-xylenol, 3,5-xylenol, 2,4,6-trimethylphenol

TABLE 12. HFET PHENOL AND ALDEHYDE EMISSION DATA

Compounds	Fuel Description and Code (EM-XXX-F)						
	Base DF-2 329	Shale Diesel Marine 453	Paraho JP-5 473	Coal Case 5A 474	Broad-cut 476	25% SRC-II 478	25% EDS 482
Phenols, mg/km							
Phenol	0.0	0.0	0.0	2.	0.0	0.0	1.
Salicylaldehyde	0.0	0.0	0.0	0.0	0.0	210.	0.5
m-Cresol +p-Cresol	1.	0.2	0.0	0.5	0.0	0.0	0.0
Group 5[a]	2.	0.5	0.0	0.9	0.0	0.4	0.0
2,3,5-trimethylphenol	0.03	0.0	0.0	0.0	0.0	0.0	0.3
2,3,5,6-tetramethylphenol	0.6	0.0	0.0	0.0	0.2	4.	8.
2-n-propylphenol	4.	8.	1.	14.	0.0	0.0	0.0
"Total"	8.	9.	1.	17.	0.2	214.	10.
Aldehydes, mg/km							
Formaldehyde	9.	8.	6.	6.	11.	0.0	1.
Acetaldehyde	1.	0.0	0.0	1.	3.	0.0	0.0
Acetone[b]	5.	3.	0.0	0.0	0.0	0.0	0.0
Hexanaldehyde	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzaldehyde	0.0	2.	7.	0.0	2.	0.0	2.
"Total"	15.	13.	13.	7.	16.	0.0	3.

[a]Group 5 consists of p-ethylphenol, 2-isopropylphenol, 2,3-xylenol, 3,5-xylenol, 2,4,6-trimethylphenol

[b]Included acrolein and propanol

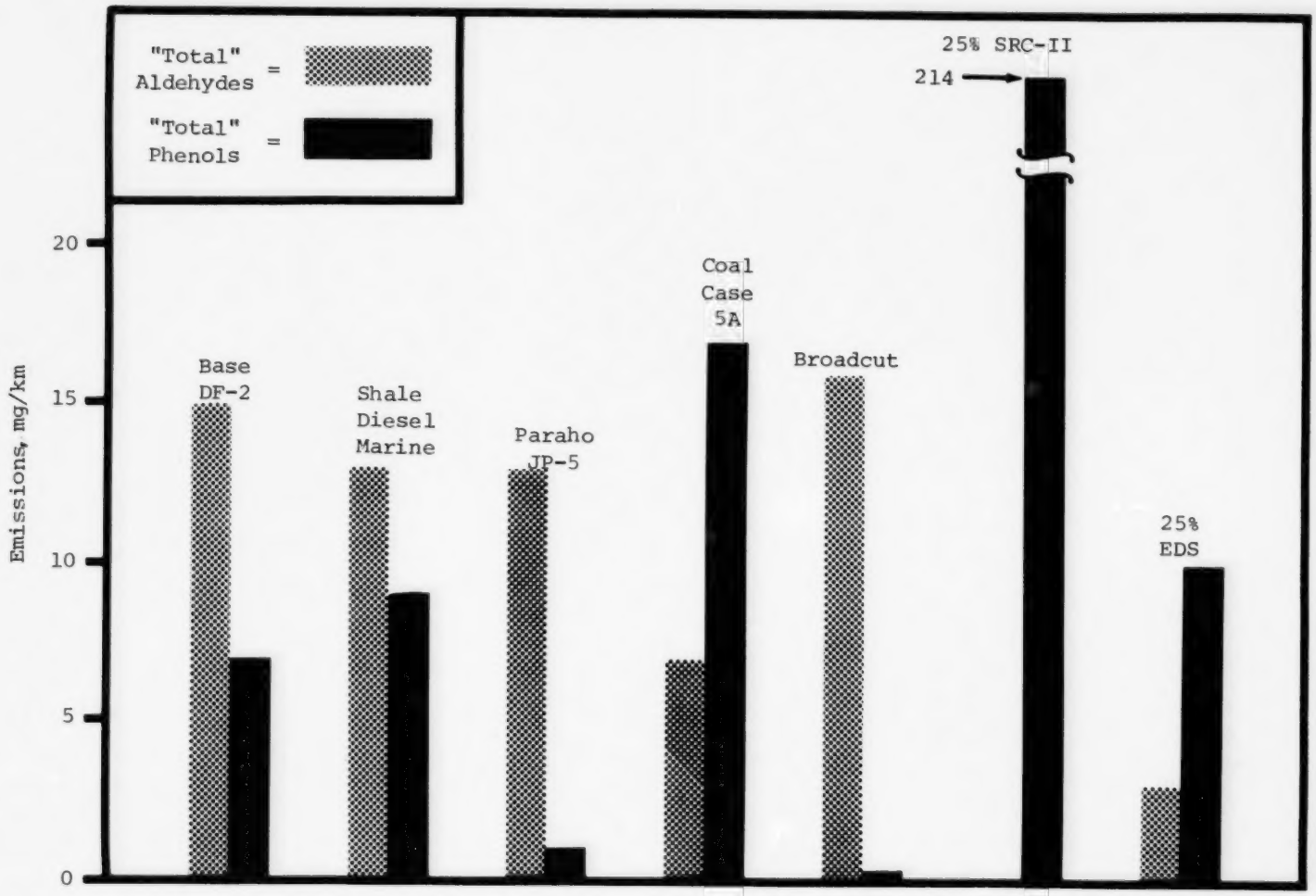

Figure 11. "Total" aldehyde and phenol emissions during HFET.

TABLE 13. RESULTS OF ODOR ANALYSIS AT STEADY-STATES

Date	Fuel Code	Fuel Type	Condition	LCA, µg/l	LCO, µg/l	TIA	
						LCA	LCO
12-12-80	EM-329-F	Base DF-2	Idle	55.	3.7	1.6	1.6
			50 kph	110.	7.5	1.8	1.9
			85 kph	400.	21.	2.2	2.3
1-19-81	EM-453-F	Shale Diesel Marine	Idle	7.5	4.4	1.0	1.6
			50 kph	23.	12.	1.4	2.1
			85 kph	60.	15.	1.6	2.2
5-6-81	EM-473-F	Paraho JP-5	Idle	9.6	1.4	1.1	1.1
			50 kph	35.	3.1	1.5	1.5
			85 kph	560.	23.	2.3	2.4
5-19-81	EM-474-F	Coal Case 5A	Idle	27.	6.3	1.4	1.8
			50 kph	76.	25.	1.7	2.4
			85 kph	160.	67.	1.9	2.8
5-27-81	EM-476-F	Broadcut	Idle	297.	13.	2.1	2.1
			50 kph	220.	12.	2.0	2.1
			85 kph	592.	53.	2.3	2.7
7-17-81	EM-478-F	25% SRC-II	Idle	143.	13.	1.9	2.1
			50 kph	17.	3.5	1.3	1.1
			85 kph	14.	3.2	1.2	1.1
8-3-81	EM-482-F	25% EDS	Idle	78.	6.5	1.5	1.8
			50 kph	360.	16.	1.7	1.2
			85 kph	129.	24.	1.5	2.4

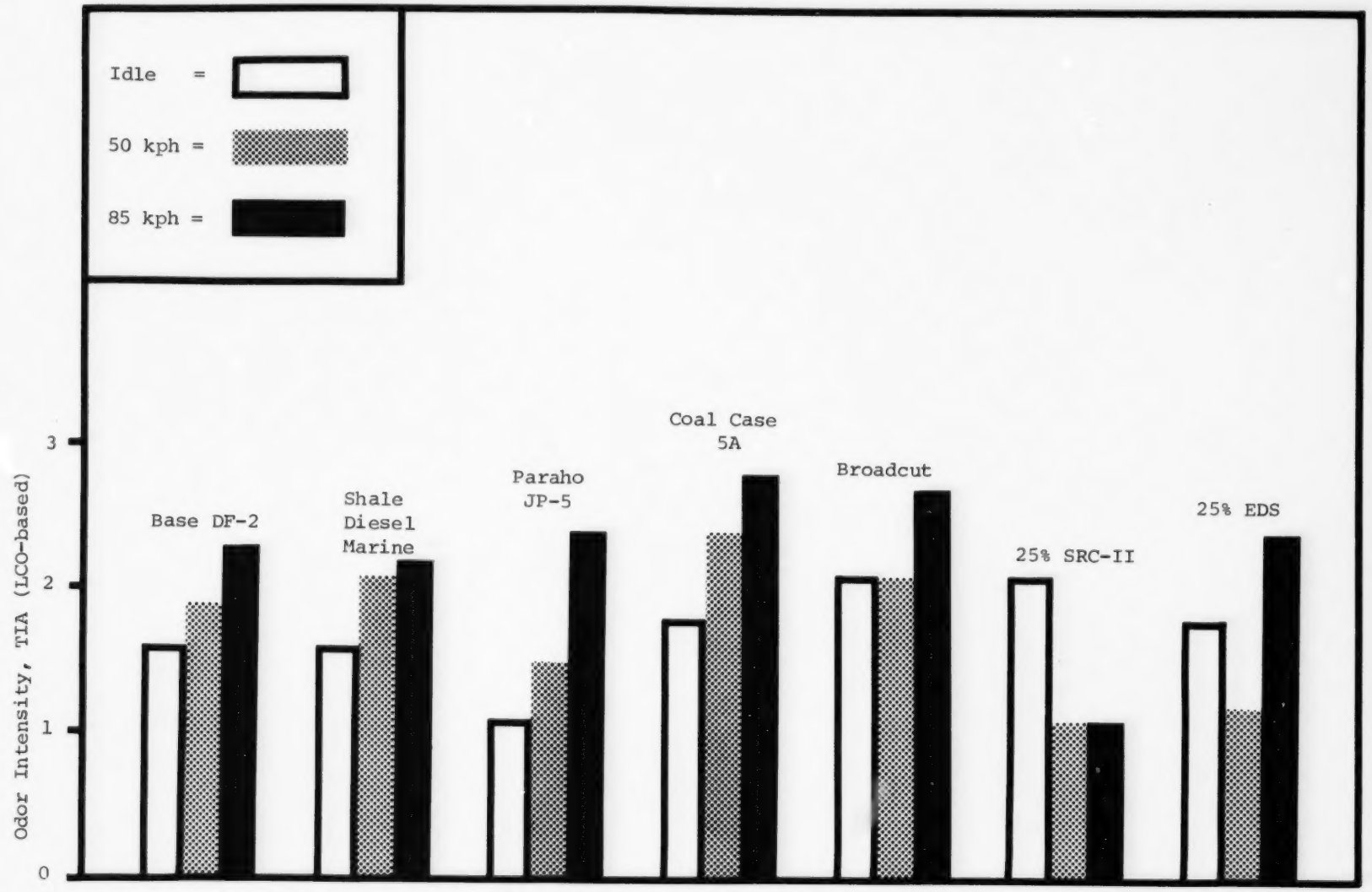

Figure 12. Odor analysis at three steady-states.

compared with the base. The 85 kph cruise results show that the Coal Case 5A and the Broadcut were associated with the highest odor levels. Lowest odor level was observed with the 25% SRC-II blend. In summary, the Broadcut and Coal Case 5A test fuels generally exhibited the highest odor levels during the three steady-state modes. Only at idle did the 25% SRC-II and 25% EDS test fuels' odor levels exceed the base fuel's. Shale diesel marine gave results similar to base fuel during the three steady-states.

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VII. SMOKE AND PARTICULATE EMISSION RESULTS

This section of the report presents summary data and discussion on visible smoke, total particulate mass emissions, particle size distribution, and particulate matter elemental analysis. In addition, it includes information on organic solubles in particulate matter, elemental analysis of the solubles, BaP in solubles, boiling range of organic solubles by gas chromatograph analysis, polarity profile of the solubles, and bioassay analysis.

A. Visible Smoke Emissions

Visible smoke was measured using an EPA-type smokemeter over the first 505 seconds (the "cold transient phase") of the FTP. Data, taken on a 2-pen strip chart recorder, consisted of vehicle speed and smoke opacity versus time. The traces, which were analyzed manually, are located in Appendix D, Pages D-2 through D-9. The results are summarized in Table 14.

TABLE 14. SUMMARY OF VISIBLE SMOKE DATA

Condition	Smoke Opacity, %, by fuel, EM-XXX-F							
	329	453	473	474	476	475	478	482
Cold Start peak	21.2	46.8	36.0	66.0	33.0	66.0	58.8	58.2
Cold idle, avg. (after start)	0.2	1.0	1.4	0.4	3.0	60.0	3.5	4.0
1st accel. peak	28.2	44.2	61.5	40.5	44.2	92.0	63.5	67.8
Idle at 125 secs, avg.	0.7	0.5	0.8	0.6	0.5	21.0	1.0	1.7
Accel. at 164 secs, peak	37.5	27.2	20.0	71.2	20.6	59.0	42.0	41.3

These data indicate rather dramatic smoke effects when running EM-475-F, the 35% SRC-II blend. Its smoke levels were very high at the start and even at the 125 second idle, by which time all the other fuels show very little smoke production at idle. Base fuel EM-329-F generally exhibited the lowest smoke levels. At the 164 second acceleration, however, several fuels did give lower smoke readings than the base fuel. Shale diesel marine (453), Paraho JP-5 (473), and the Broadcut (476) all showed reduced smoke at the

164 second acceleration. With the exception of the 35% SRC-II, the greatest smoke level increases were generally associated with the other test fuels containing coal-derived liquids; Coal Case 5A (474), 25% SRC-II (478), and 25% EDS (482). Smoke levels for the two blends containing 25% coal-derived middle distillate (from different processes), 478 and 482, are almost identical.

B. Particulate Mass Emissions

Particulate mass emissions during the two transient cycles and the three steady-states are summarized in Table 15. Individual run data are located on the computer printouts in Appendix C. FTP and HFET results are presented graphically in Figure 13. The trends by fuel are similar for both operating cycles except for the 25% SRC-II. The 25% SRC-II particulate mass rate was 56 percent above the base fuel rate during the FTP, but the rates were the same during the HFET. One possibility is that the combustion of the SRC-II material improves as the vehicle warms up. Particulate mass emission increases were observed with the Coal Case 5A, and to a lesser extent with the EDS blends. These results are not unexpected, based on an earlier study.[3] In that study, a regression equation for particulate mass emissions from a single vehicle was formulated. Particulate increases were associated with fuel aromatic content and fuel nitrogen increases. The 25% SRC-II blend had the highest aromatic and nitrogen levels of the blends tested. As stated earlier in the report, the 25% EDS naphtha test blend was evaluated only on selected cycles, and for selected emissions. Broadcut fuel decreased particulate emission 16 percent during the FTP, and 32 percent during the HFET as compared with the base. The poor combusion characteristics of the 35% SRC-II are shown in Table 15 as a significant particulate increase. Filter plugging prevented further testing of this material.

TABLE 15. AVERAGE PARTICULATE MASS EMISSION DATA

Fuel Code	Fuel Type	Grams Particulate per Kilometer				
		Calculated 1981 FTP	HFET	Steady-State		
				Idle[a]	50 kph	85 kph
EM-329-F	Base DF-2	0.25	0.25	0.71	0.17	0.28
EM-453-F	Shale Diesel Marine	0.27	0.27	0.60	0.18	0.36
EM-473-F	Paraho JP-5	0.25	0.26	0.48	0.08	0.26
EM-474-F	Coal Case 5A	0.32	0.35	1.14	0.14	0.46
EM-476-F	Broadcut	0.21	0.17	0.84	0.08	0.20
EM-475-F	35% SRC-II	2.06[b]	----	----	----	----
EM-478-F	25% SRC-II	0.39	0.24	1.53	0.13	0.24
EM-482-F	25% EDS	0.28	0.28	1.05	0.17	0.28
EM-485-F	25% EDS Naphtha	0.30	----	----	----	----

[a] Emissions in g/h instead of g/km
[b] Calculated on basis of cold 505 data

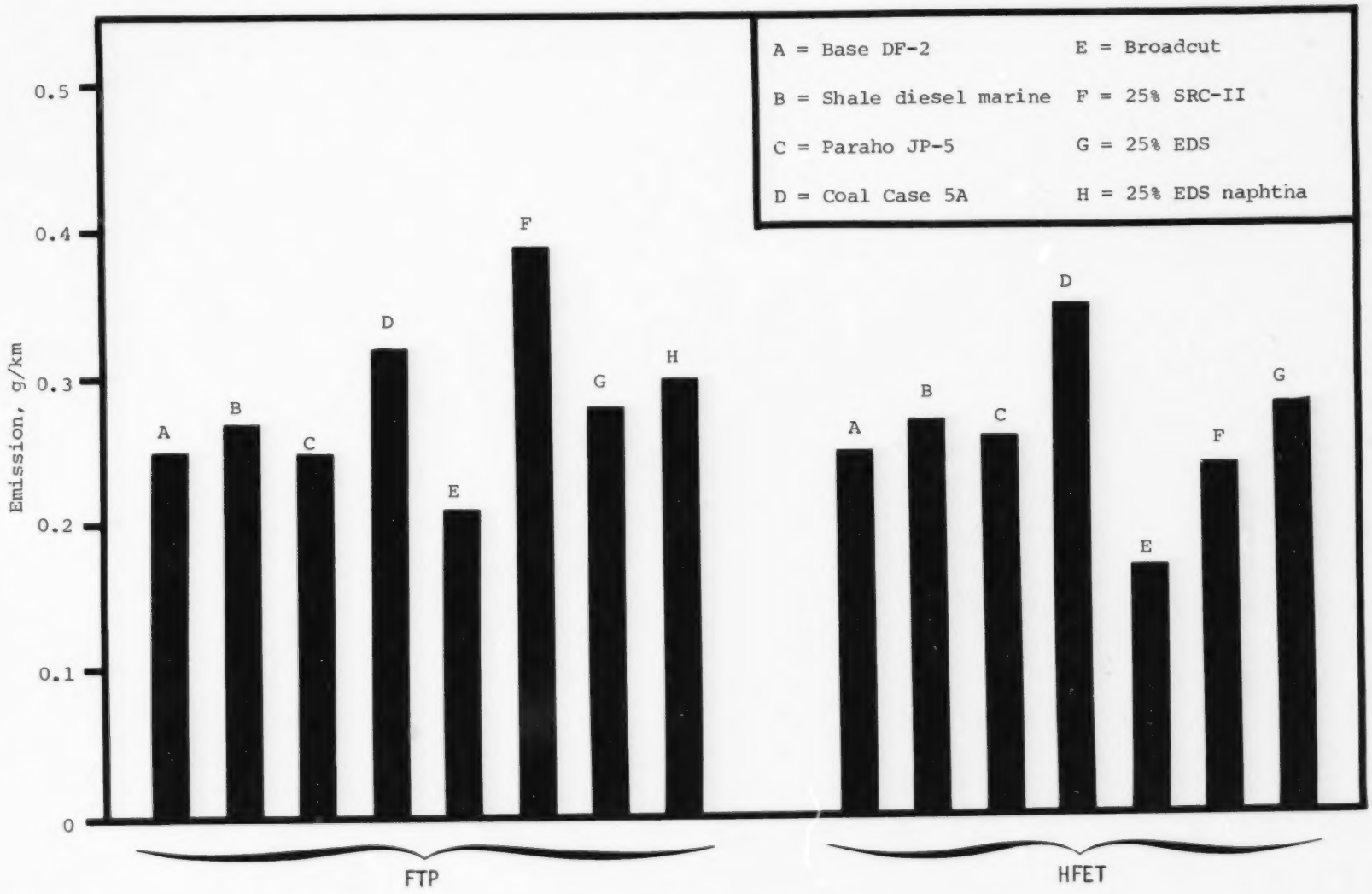

Figure 13. Particulate mass emissions during FTP and HFET cycles.

Steady-state data show that the idle mode is the chief contributor to the increases observed in the FTP data for the coal-derived liquid blends (Coal Case 5A, 25% SRC-II, and the two EDS fuels). These data also help to explain the particulate emission decreases for 25% SRC-II from the FTP to the HFET. At higher speeds the 25% SRC-II particulate emissions are lower than the base fuel.

C. Particulate Size Distribution

Data from impactor runs were analyzed and are presented as percent of the total particulate mass by stage in Table 16. Table 16 shows that in most cases, over half the particulate mass was composed of particles smaller than 0.2 μm. Coal Case 5A generated the smallest particles (about 90 percent <0.2 μm). Largest particles were seen with the 35% SRC-II blend, although these particles were collected only during the cold 505 seconds of the FTP; while the other samples were collected during an entire "4-bag" FTP.

Table 17 lists the particle size distributions as cumulative mass percent smaller than stage cutoff diameter, and these data are shown graphically in Figure 14. This graph indicates a fairly wide variation in size distributions by fuel, with a substantial fraction of the variation occurring on the back-up filter. The 25% EDS blend generated about the same distribution of particle sizes as the 25% SRC-II blend.

D. Analysis of Particulate Composition

This subsection includes data on major elements and trace elements. Carbon and hydrogen analyses were performed on particulate collected using 47 mm glass fiber filters. Particulate collected on 47 mm Fluoropore filters was analyzed for trace elements.

Carbon and hydrogen data are listed in Table 18. As seen in an earlier study[3], the data show fairly high carbon content, indicative of "dry" or soot-like particulate material in most cases. The 25% SRC-II blend gave somewhat lower carbon percentage in particulates, indicating a more oily material. The hydrogen content of this particulate sample, however, does not support the oily material supposition. The technique used to analyze carbon and hydrogen content of particulate collected on glass fiber filters appears somewhat questionable based on these results and others.[3,6] A new procedure is needed to insure correct and accurate analysis of particulate collected on glass fiber filters.

Data on trace elements are given in Appendix D, page D-10. As a whole, these elements made up 0.3% to 1.6% of the particulate mass. The trace elements found most commonly in the particulate matter were sulfur, iron, nickel, calcium, and zinc. Possible sources of iron and nickel are wear products from the engine and exhaust system. Sulfur, calcium, and zinc can probably be attributed to

TABLE 16. PARTICULATE SIZE DISTRIBUTION

Fuel Code	Fuel Description	Percent of Total Particulate									Vehicle Total Particulate g/cycle[a]
		Stage 3 9.5 µm[a]	Stage 4 5.8 µm[a]	Stage 5 3.7 µm[a]	Stage 6 2.1 µm[a]	Stage 7 1.2 µm[a]	Stage 8 0.8 µm[a]	Stage 9 0.5 µm[a]	Stage 10 0.2 µm[a]	Filter	
EM-329-F	Base DF-2	4.9	2.7	6.3	4.4	8.2	5.0	6.1	7.9	55.	5.81
EM-329-F	Base DF-2	6.8	6.3	2.0	2.3	5.7	2.3	2.7	6.7	65.	6.05
EM-453-F	Shale Diesel Marine	2.0	2.7	0.91	1.8	2.9	4.2	3.3	2.6	80.	6.58
EM-473-F	Paraho JP-5	0.0	3.0	8.0	8.0	5.0	4.1	9.1	0.0	63.	6.00
EM-474-F	Coal Case 5A	0.70	3.7	0.0	1.8	1.4	0.0	0.87	0.0	92.	7.80
EM-474-F	Coal Case 5A	0.0	0.90	0.68	4.9	4.2	0.23	0.0	0.0	89.	7.82
EM-476-F	Broadcut	3.1	3.7	3.8	5.1	3.6	3.6	2.3	0.0	75.	5.12
EM-475-F	35% SRC-II	1.5	2.2	2.4	3.6	2.9	8.3	23.	16.	40.	17.85[b]
EM-478-F	25% SRC-II	5.2	3.6	2.7	3.9	7.2	4.4	5.9	6.8	60.	8.49
EM-482-F	25% EDS	2.1	3.1	2.7	4.6	4.8	3.8	3.8	7.0	68.	7.12

[a]based on 47 mm Pallflex for 4-bag FTP
[b]based on 903 seconds of first FTP only

TABLE 17. CUMULATIVE PARTICLE SIZE DISTRIBUTION DURING COLD AND HOT FTP

Fuel Code	Fuel Description	Cumulative Percent of Total Particulate									Vehicle Total Particulate g/cycle[a]
		Stage 3 9.5 µm[a]	Stage 4 5.8 µm[a]	Stage 5 3.7 µm[a]	Stage 6 2.1 µm[a]	Stage 7 1.2 µm[a]	Stage 8 0.8 µm[a]	Stage 9 0.5 µm[a]	Stage 10 0.2 µm[a]	Filter	
EM-329-F	Base DF-2	100.5	95.6	92.9	86.6	82.2	74.0	69.0	62.9	55.	5.81
EM-329-F	Base DF-2	99.8	93.0	86.7	84.7	82.4	76.7	74.4	71.7	65.	6.05
EM-453-F	Shale Diesel Marine	100.4	98.4	95.7	94.8	93.0	90.1	85.9	82.6	80.	6.58
EM-473-F	Paraho JP-5	100.2	100.2	97.2	89.2	81.2	76.2	72.1	63.0	63.	6.00
EM-474-F	Coal Case 5A	100.5	99.8	96.1	96.1	94.3	92.9	92.9	92.0	92.	7.80
EM-474-F	Coal Case 5A	99.9	99.9	99.0	98.3	93.4	89.2	89.0	89.0	89.	7.82
EM-476-F	Broadcut	100.2	97.1	93.4	89.6	84.5	80.9	77.3	75.0	75.	5.12
EM-475-F	35% SRC-II	99.9	98.4	96.2	93.8	90.2	87.3	79.0	56.0	40.	17.85[b]
EM-478-F	25% SRC-II	99.7	94.5	90.9	88.2	84.3	77.1	72.7	66.8	60.	8.49
EM-482-F	25% EDS	99.9	97.8	94.7	92.0	87.4	82.6	78.8	75.0	68.	7.12

[a]based on 47 mm Pallflex for 4-bag FTP
[b]based on 903 seconds of first FTP only

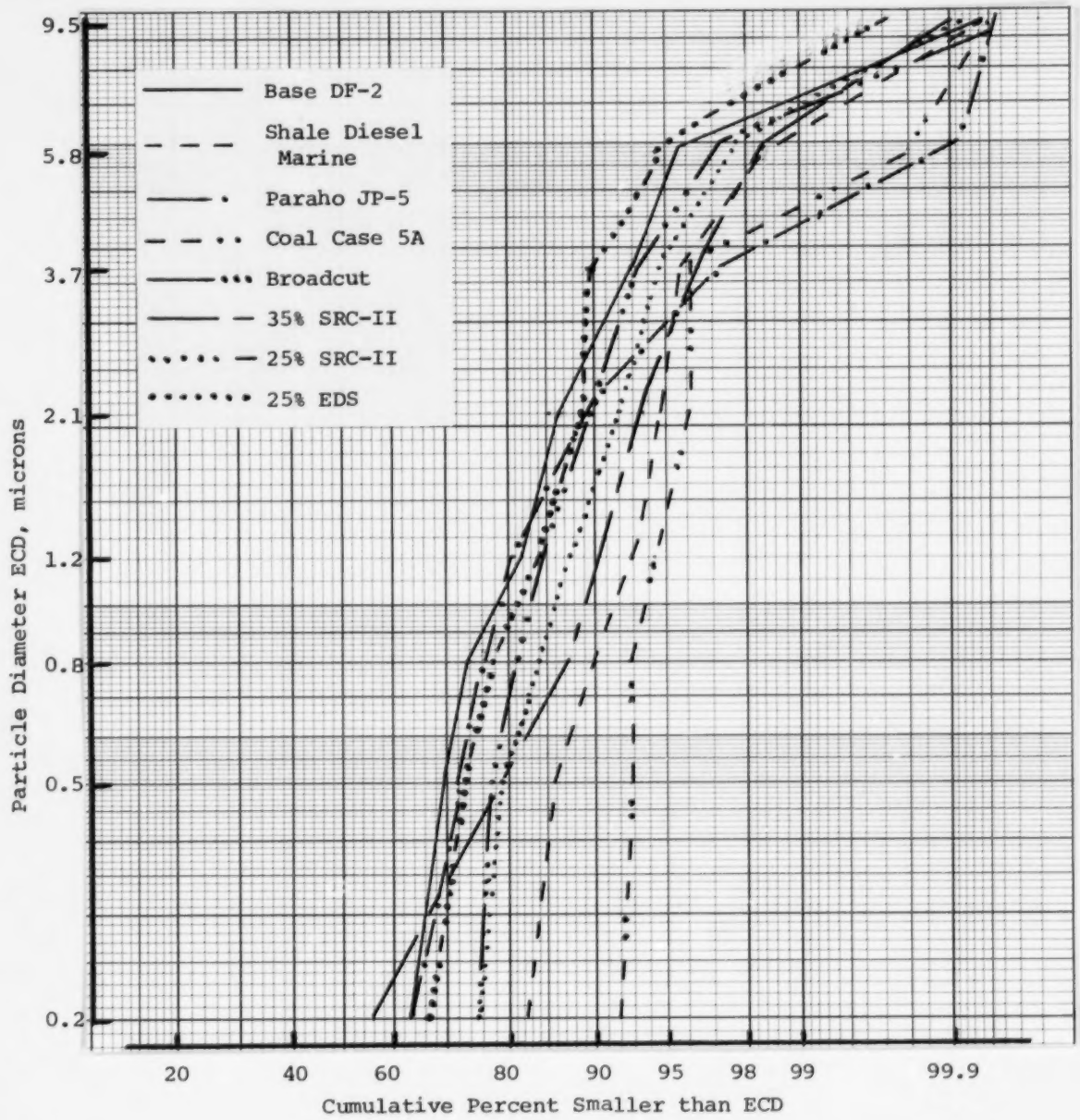

Figure 14. Cumulative particle size distributions by impactor.

TABLE 18. CARBON AND HYDROGEN IN EXHAUST PARTICULATE MATTER

Fuel Code	Fuel Description	Cycle	Weight Percent		Vehicle Total Particulate, g/test[a]
			Carbon	Hydrogen	
EM-329-F	base DF-2	FTPc	81.6	2.89	2.708
		FTPh	80.3	2.73	2.575
		HFET	83.6	2.95	2.512
EM-453-F	shale diesel marine	FTPc	84.8	2.53	3.630
		FTPh	86.6	2.30	2.556
		HFET	91.0	2.05	3.882
EM-473-F	Paraho JP-5	FTPc	88.6	2.32	2.949
		FTPh	90.8	2.74	2.104
		HFET	93.7	2.39	3.359
EM-474-F	Coal Case 5A	FTPc	87.5	2.02	3.507
		FTPh	88.2	2.28	2.817
		HFET	87.4	1.76	5.117
EM-476-F	Broadcut	FTPc	83.3	2.91	2.505
		FTPh	78.1	3.13	1.941
		HFET	77.9	3.00	2.512
EM-478-F	25% SRC-II	FTPc	68.8	3.14	2.677
		FTPh	65.9	2.20	2.129
		HFET	41.9	0.97	3.444
EM-482-F	25% EDS	FTPc	78.9	1.75	3.943
		FTPh	82.5	2.00	2.921
		HFET	84.3	4.96	4.569

[a]Based on 47 mm Pallflex

fuel sulfur and lubricating oil additives. The 25% SRC-II blend was associated with measureable amounts of lead, manganese and bromine in the hot FTP and HFET, while samples taken with the other fuels exhibited little of these elements, if any.

E. Composition of Organic Solubles in Particulate Matter

The organic soluble portion of the particulate was obtained from particulate samples collected on 20x20 inch Pallflex filters, using Soxhlet extraction procedures (methylene chloride as solvent). The amounts of organic solubles extracted are presented in Table 19 as percent of the total particulate mass. This result gives an indication of the split between soot and condensed organics in the total particulate matter. During the FTP, the Broadcut and 25% SRC-II test fuels generated particulate with substantially higher solubles than the base fuel (25% vs 18%). These values indicate a more oily particulate, possibly containing more unburned fuel. Gaseous hydrocarbon increases were also seen with these two fuels, supporting this supposition. During the HFET, the Broadcut again increased the amount of organic solubles; but the 25% SRC-II gave about the same levels as the base fuel. The 25% EDS naphtha generated particulate matter with solubles lower than those for the base fuel during both the FTP and the HFET.

A portion of the organic soluble material was analyzed for carbon and hydrogen. The results are given in Table 19. All the elemental data are indicative of hydrocarbon-like materials (numeric H/C ratio between 1.79 and 1.83). Overall, there is no appreciable difference between the seven fuels or the two cycles regarding carbon and hydrogen content of the resulting organic solubles.

F. Gas Chromatograph "Boiling Range" Analysis of Organic Solubles

The organic soluble portion of particulate matter resembles a very heavy oil or a varnish. A high-temperature GC-simulated boiling point distribution, with an internal standard, was determined by an analysis of organic soluble material from particulate generated with each fuel. Table 20 summarizes the results for samples generated during both the FTP and HFET. The chromatograms for each of the samples summarized in Table 20, along with an example analysis of a crude oil and a calibration run, are located in Appendix D, Figures D-9 through D-25.

FTP results show that solubles from tests on the Broadcut, 25% SRC-II and 25% EDS test fuels show slightly lower boiling ranges as compared with the base fuel for the first 40%. The percent recovery for the solubles indicates that in some cases, a sizeable amount of material (over 30 percent) boils over 640°C. Based on recoveries, Broadcut fuel yielded the largest amount of organic solubles boiling under 640°C. Most of the test fuels emitted more organic soluble compounds whose boiling points were under 640°C for the HFET than for the FTP. Over ninety percent of the compounds generated using

TABLE 19. COMPOSITION OF ORGANIC SOLUBLES FROM PARTICULATE MATTER

Fuel Code	Fuel Description	Cycle[b]	Weight Percent		Vehicle Total Solubles, g/test[a]	% of Total Particulate
			Carbon	Hydrogen		
EM-329-F	base DF-2	FTP	85.2	12.9	1.150	18.0
		HFET	85.5	12.9	0.810	18.0
EM-453-F	shale diesel marine	FTP	85.6	13.0	1.098	17.7
		HFET	85.7	13.0	0.838	17.0
EM-473-F	Paraho JP-5	FTP	85.4	13.1	0.801	12.2
		HFET	85.6	13.0	0.661	16.4
EM-474-F	Coal Case 5A	FTP	85.6	12.9	1.488	17.6
		HFET	85.6	13.0	0.750	12.0
EM-476-F	Broadcut	FTP	85.5	13.0	1.181	25.2
		HFET	85.2	12.9	0.682	23.9
EM-478-F	25% SRC-II	FTP	85.3	12.8	1.771	25.6
		HFET	85.0	13.0	0.658	16.4
EM-482-F	25% EDS	FTP	84.8	12.8	0.955	13.1
		HFET	85.5	13.0	0.602	12.7

[a] based on 20x20 Pallflex filters
[b] "4-bag" FTP's

TABLE 20. CHROMATOGRAPH ANALYSIS OF ORGANIC SOLUBLES IN PARTICULATE MATTER

	Boiling Temperature, °C, at Distillation Point by Fuel during 4-bag FTP						
Fuel Description	Base DF-2	Shale Diesel Marine	Paraho JP-5	Coal Case 5A	Broadcut	25% SRC-II	25% EDS
Fuel Code	EM-329-F	EM-453-F	EM-473-F	EM-474-F	EM-476-F	EM-478-F	EM-482-F
IBP	318	307	337	307	235	249	251
10% point	365	358	374	357	357	347	357
20% point	388	379	397	376	381	367	377
30% point	416	402	422	396	401	389	396
40% point	451	429	451	425	422	427	421
50% point	494	463	482	472	449	495	455
60% point	537	499	510	525	493	581	497
70% point	605	531	548	--	539	--	539
80% point	--	603	--	--	599	--	611
90% point	--	--	--	--	--	--	--
EP	--	--	--	--	--	--	--
Recovery @ 640°C	70.0	80.1	77.5	67.0	86.0	65.0	82.8
	Boiling Temperature, °C, at Distillation Point by Fuel during HFET						
Fuel Code	EM-329-F	EM-453-F	EM-473-F	EM-474-F	EM-476-F	EM-478-F	EM-482-F
IBP	325	314	236	336	239	242	238
10% point	374	365	367	378	363	358	363
20% point	400	384	394	399	387	385	384
30% point	429	409	419	422	410	412	407
40% point	462	436	446	445	435	442	432
50% point	492	469	471	471	466	476	461
60% poiny	526	503	498	495	500	510	490
70% point	582	549	526	520	537	552	520
80% point	--	--	572	569	600	611	566
90% point	--	--	630	--	--	--	639
EP	--	--	--	--	--	--	--
Recovery @ 640°C	71.7	78.8	91.4	85.6	84.6	83.6	90.2

Paraho JP-5 and 25% EDS middle distillate boiled under 640°C. This fraction is high compared to the 72 percent base fuel value.

G. Fractionation by Relative Polarity

Composition of the soluble organic fraction of the particulate is complex, and its separation into individual compounds is very difficult. Fractionation of the organic solubles by high performance liquid chromatography (HPLC) separates the soluble portion into a series of fractions of increasing molecular polarity. This procedure[15] is not quantitative, but provides a method to collect fractions with generally different polarities. All samples were analyzed at the same time, having the same ratio of organic extract and carrier solvent. Therefore, the results can be compared to one another on a relative basis to estimate increases or decreases of compound classes which differ from each other by molecular polarity. Figure 15 through 22 show the HPLC chromatographic outputs for direct comparison of the relative response of increasingly polar compounds at the wavelengths discussed in Section IV, Part E-5 of the report.

Each figure contains three traces, one representing the carrier solvent composition, a second representing the ultraviolet detector response, and the third representing the fluorescence detector response. Figure 15 shows the response of BaP and 9-fluorenone. BaP and similar compounds elute in this non-polar region. Near the end of the transition period (i.e., solvent polarity now polar) 9-fluorenone elutes. With 100 percent methylene chloride, even more polar compounds elute. For example, acridine elutes during this polar period (at about 70 minutes).

A CRC study[15] indicated that compounds which fluoresce in the transition fraction (i.e. 20 to 30 minutes elution time, which is a fraction of intermediate polarity) yielded the highest Ames response (i.e. mutagenic activity). During this period, 20.9 percent of the Ames activity was associated with 2.5 weight percent of the organic soluble material. Figures 16 through 22 show that the greatest fluorescence response in this fraction (20 to 30 minutes elution time) was associated with the Paraho JP-5. The Broadcut and Coal Case 5A fuels also showed a high fluorescence response in this fraction. On the other hand, the 25% EDS material did not yield any response in this fraction, while the base fuel responded only slightly. The 25% SRC-II blend gave a peak shape similar to the Broadcut and Coal Case 5A fuels, but with a smaller total area. In summary, based on the results of the aforementioned CRC data, increases in Ames activity as compared to the base fuel may be observed for all the fuels except the 25% EDS blend.

In the period between 2 and 10 minutes elution time, polynuclear compounds, which are relatively non-polar (such as BaP), elute. Several of these compounds are mutagenic. The particulate extract from all of the test fuels show high UV fluorescence response in this fraction. The 25% EDS blend

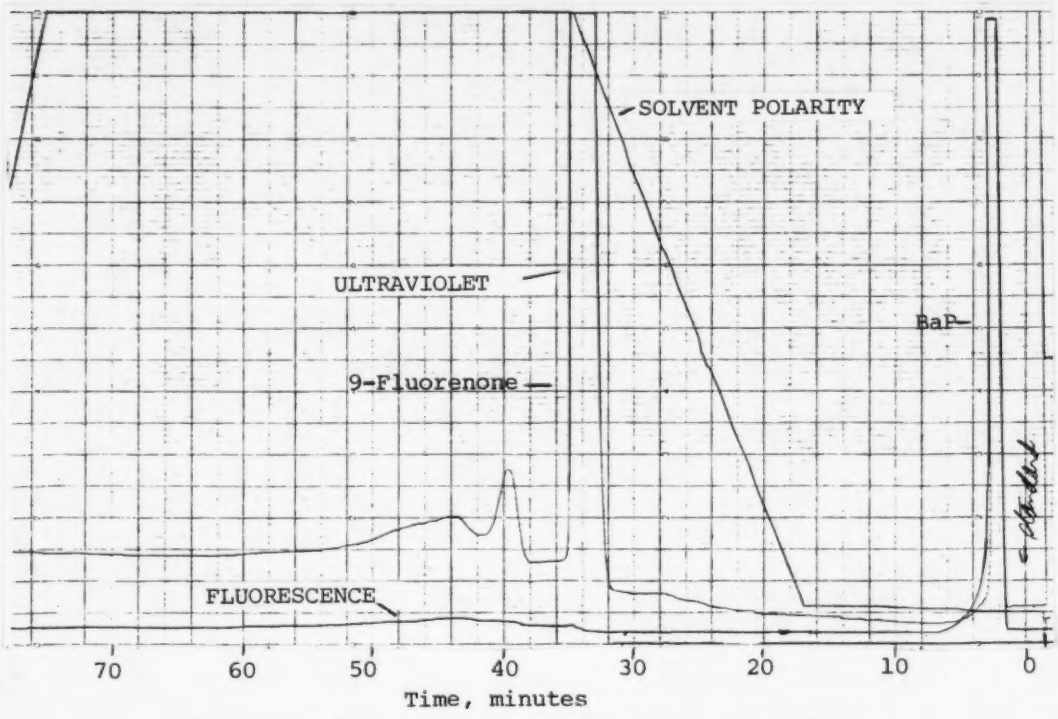

Figure 15. HPLC response to BaP and 9-fluorenone.

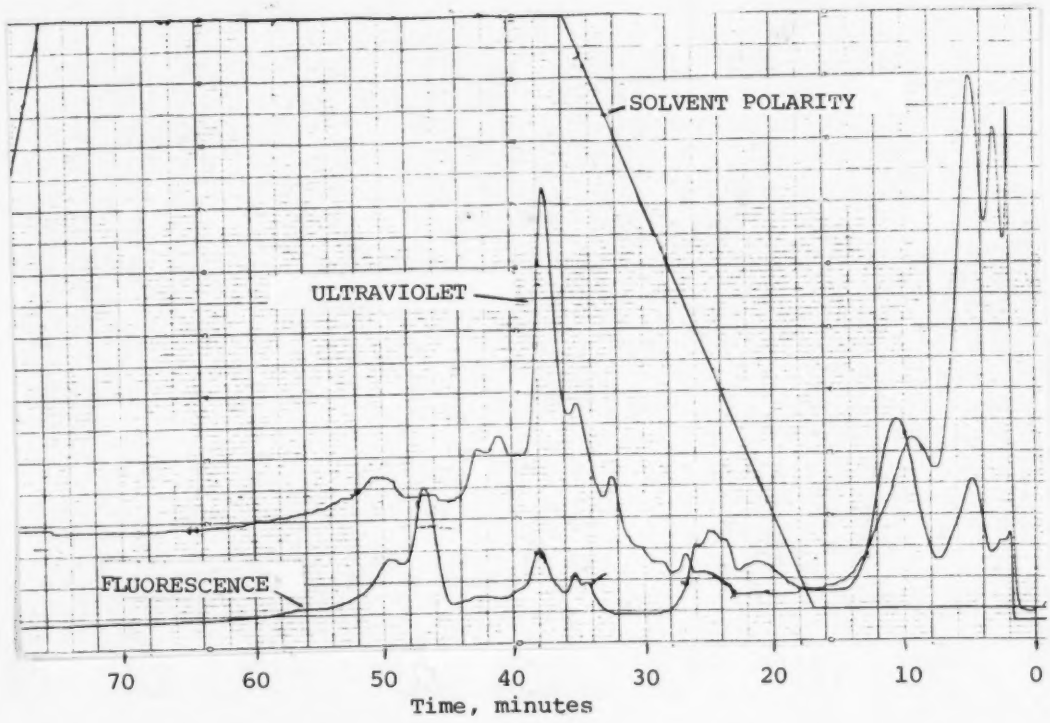

Figure 16. HPLC response to extract generated from Base DF-2.

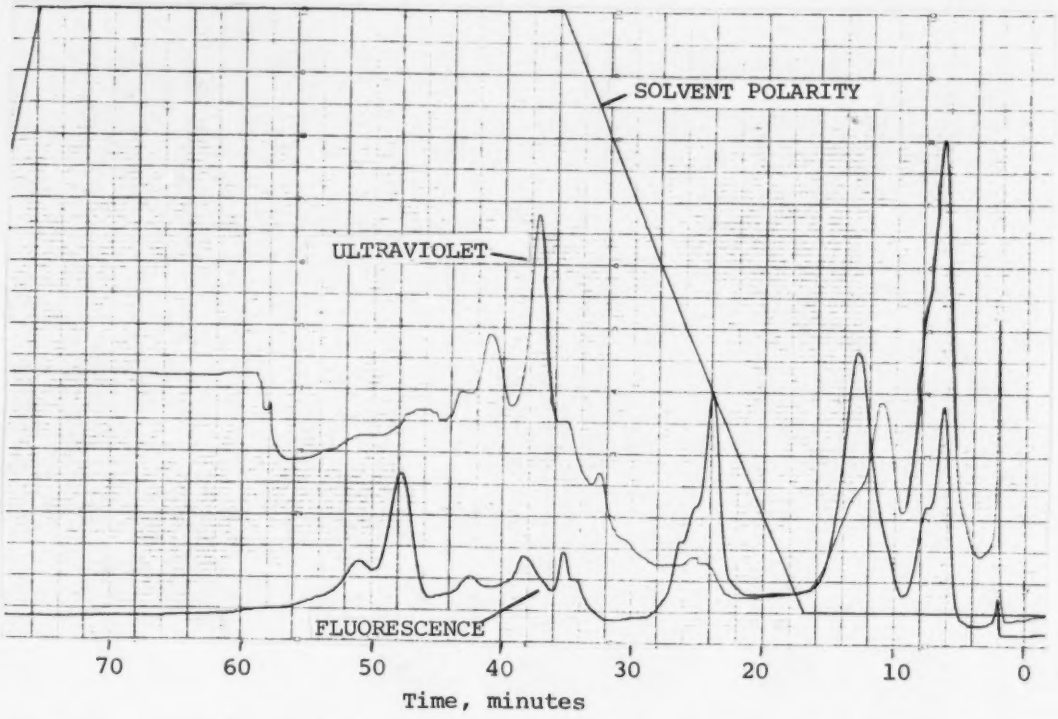

Figure 17. HPLC response to extract generated from Shale Diesel Marine.

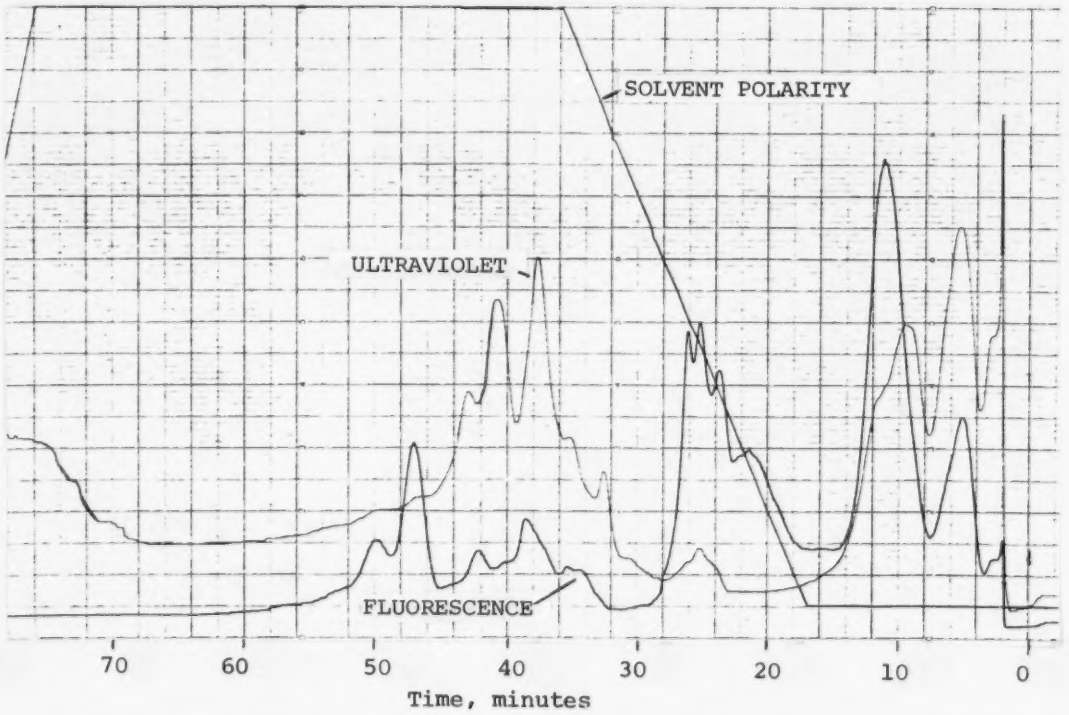

Figure 18. HPLC response to extract generated from Paraho JP-5.

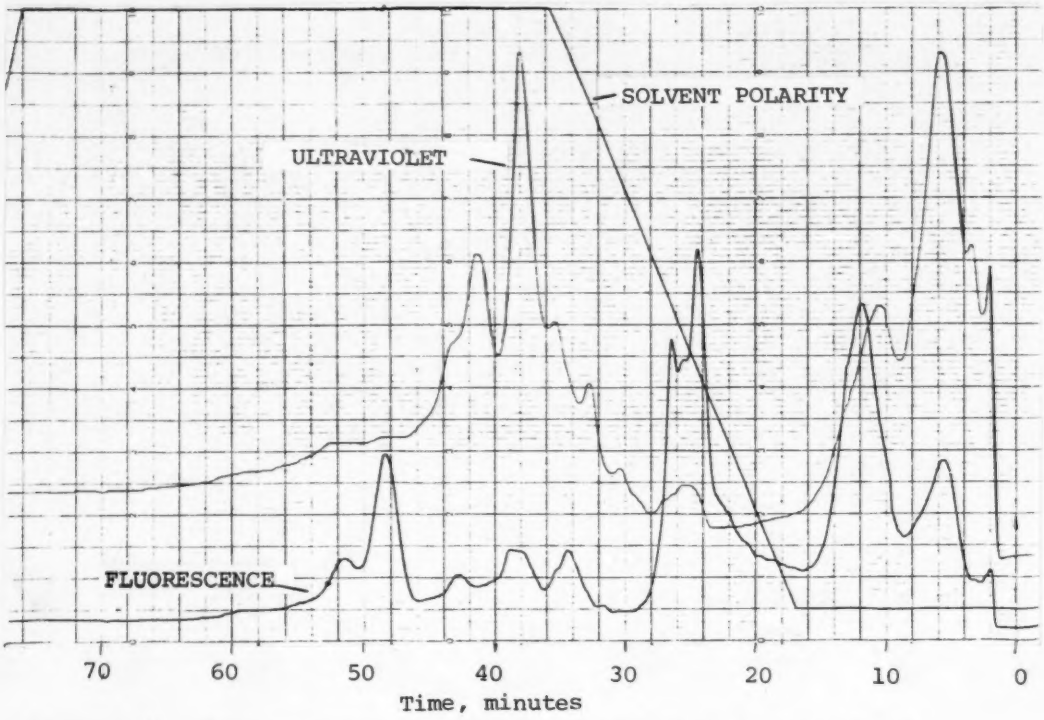

Figure 19. HPLC response to extract generated from Coal Case 5A.

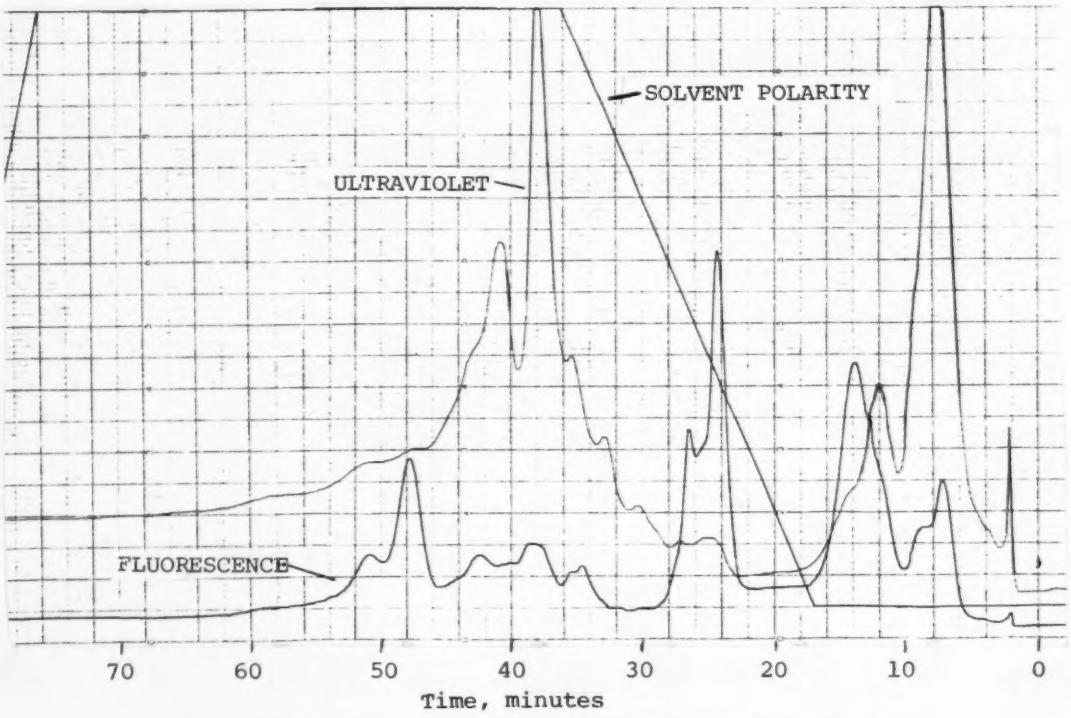

Figure 20. HPLC response to extract generated from Broadcut.

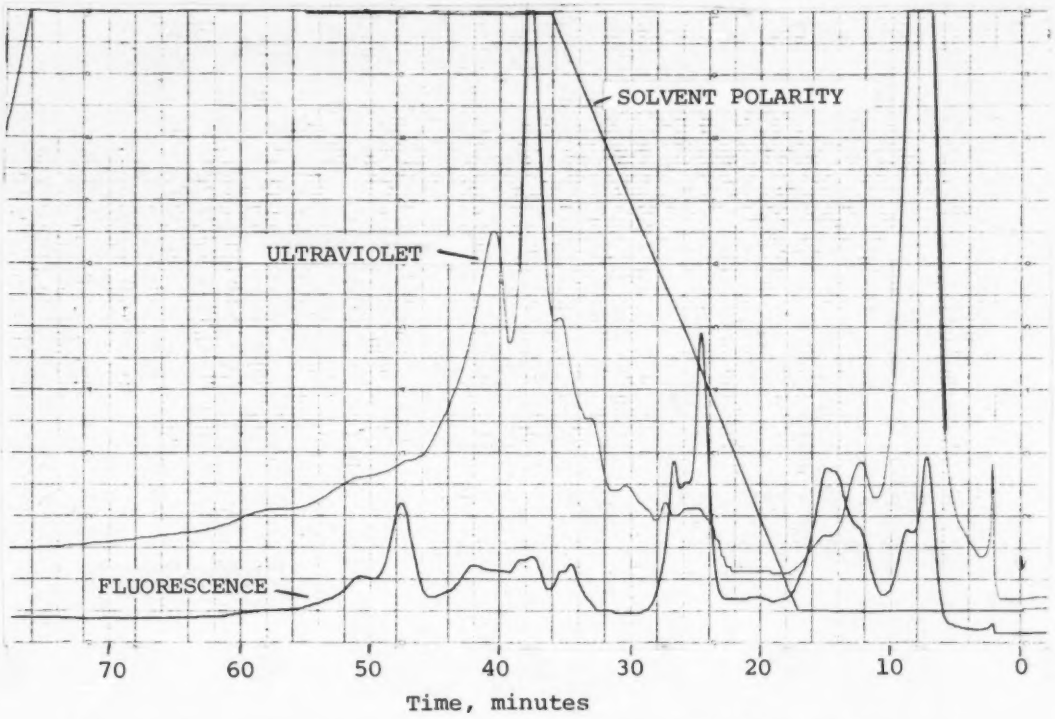

Figure 21. HPLC response to extract generated from 25% SRC-II.

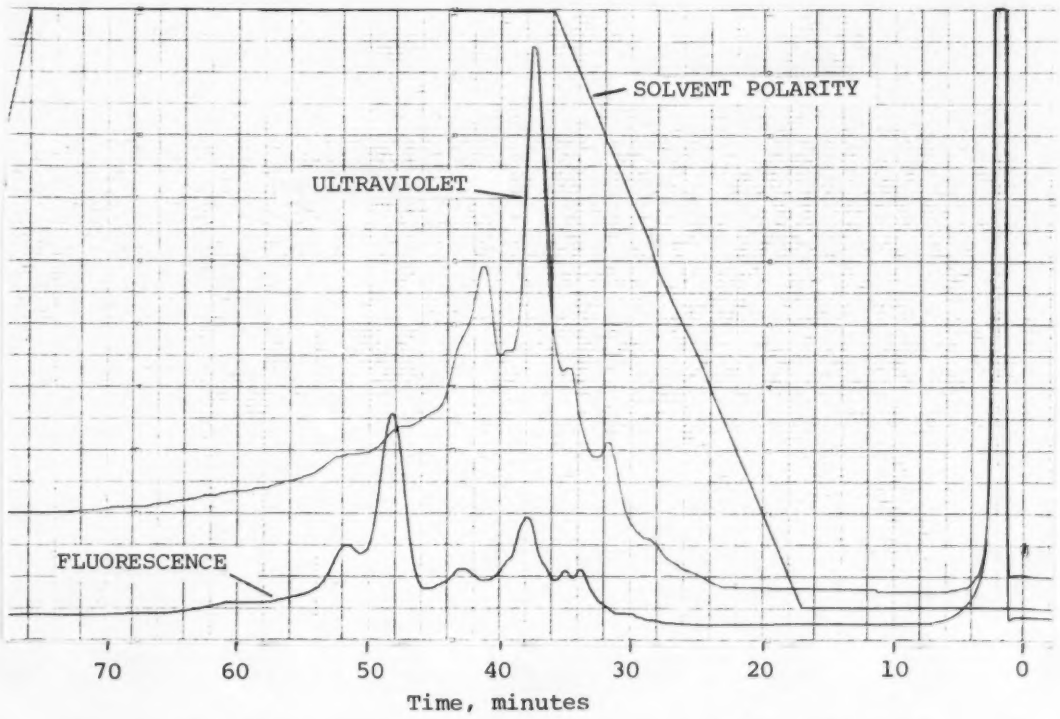

Figure 22. HPLC response to extract generated from 25% EDS.

responses appear different from any of the other samples in this fraction with a single large fluorescence peak and no UV activity, reminiscent of the run with compounds shown in Figure 15. Treating the entire HPLC chromatograms as "fingerprints", it is interesting to note that Coal Case 5A and the Broadcut fuel generated almost identical traces.

H. Benzo(a)pyrene (BaP) in Organic Solubles

BaP results are presented in Table 21, and are shown graphically in Figure 23. The BaP present in the organic soluble portion of the particulate for the fuels tested is substantially higher (about a factor of 10) than that found in other studies.[3,6,17] Time was spent to verify these results by checking the procedure, solvents, calculations, and parameters. This group of samples was also run between samples generated on other in-house studies. The results of the samples that bracketed this study's samples indicated typically low BaP values, substantiating the unexpectedly high values for this test vehicle. HPLC analyses showed a large amount of non-polar polynuclear compounds similar to BaP.

TABLE 21. BaP PRESENT IN ORGANIC SOLUBLES DURING $FTP_c + FTP_h$

Fuel Code	Fuel Description	Filter No. 5830.3-	Part. Rate, g/km[a]	% Organic Extract.	% BaP in Extract	BaP Rate µg/km
EM-329-F	base DF-2	P20-82,83	0.25	14.6	0.042	14.9
EM-453-F	shale diesel marine	P20-48,49	0.32	14.8	0.071	34.0
EM-473-F	Paraho JP-5	P20-57,58	0.27	13.6	0.087	31.6
EM-474-F	Coal Case 5A	P20-69,70	0.34	15.0	0.085	44.1
EM-476-F	Broadcut	P20-72,73	0.23	25.0	0.053	30.2
EM-478-F	25% SRC-II	P20-98,99	0.28	20.7	0.017	10.0
EM-482-F	25% EDS	P20-107,108	0.34	14.6	0.050	24.3
EM-485-F	25% EDS naphtha	P20-111,112	0.29	12.7	0.023	8.7

[a]based on 20x20 Pallflex filters

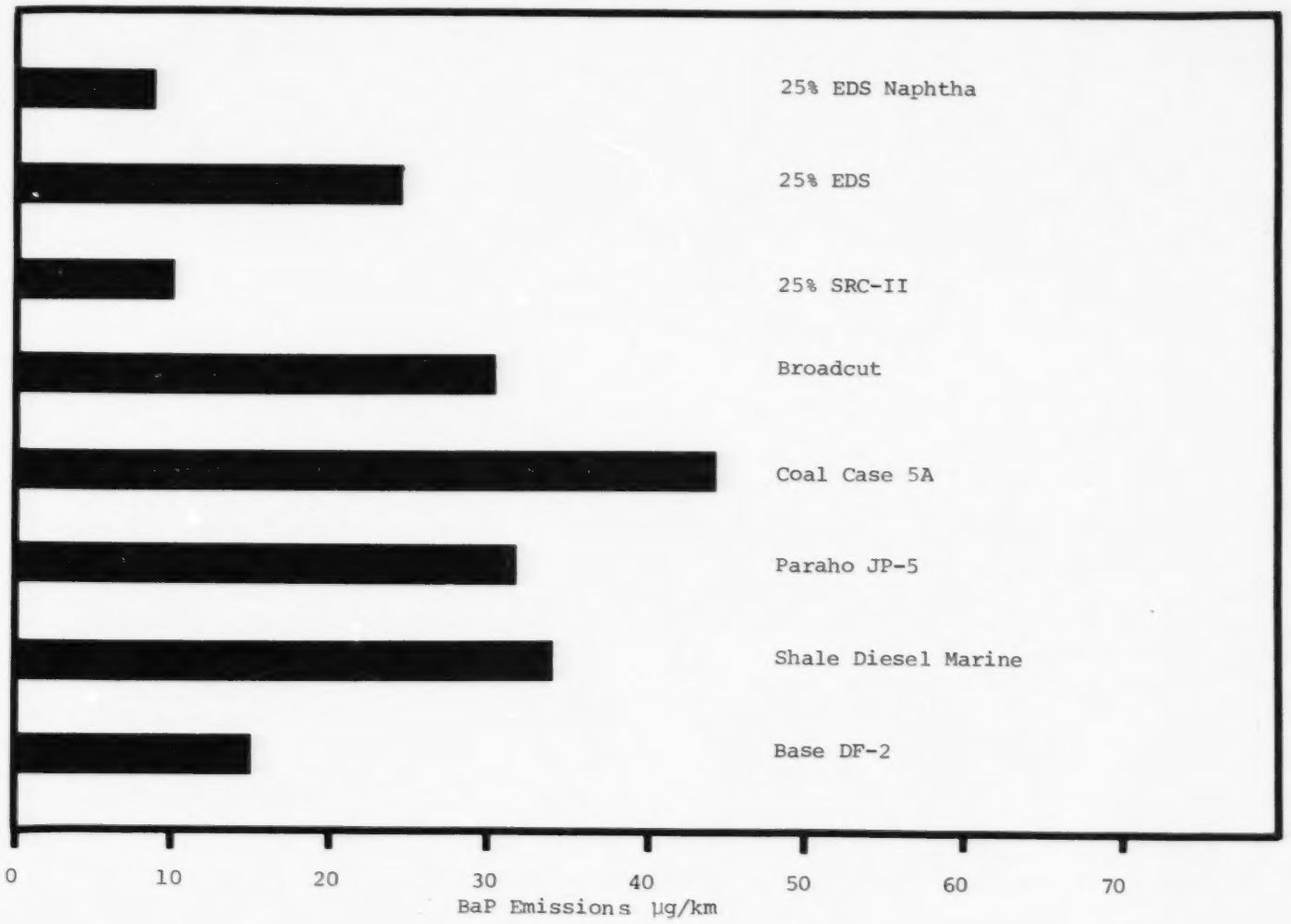

Figure 23. BaP emissions during FTP.

The largest BaP emissions was associated with the Coal Case 5A fuel about 3 times higher than for the base fuel. Values up to twice the base fuel level were seen with the Shale Diesel, Paraho JP-5, Broadcut, and 25% EDS. Slight reductions were observed with the 25% EDS Naphtha and 25% SRC-II. Comparing the 25% EDS middle distillate with the 25% SRC-II shows that the 25% EDS produced twice the BaP associated with the 25% SRC-II. However, a lighter cut of the EDS material, 25% EDS naphtha, resulted in approximately the same BaP emissions at the 25% SRC-II.

I. Mutagenic Activity by Ames Testing

The Ames test, as employed in this program, refers to a bacterial mutagenesis plate assay with Salmonella typhimurium according to the method of Ames.[14] This bioassay determines the ability of chemical compounds or mixtures to cause mutation of DNA in the bacteria, positive results occurring when histidine-dependent strains of bacteria revert (or are mutated) genetically to forms which can synthesize histidine on their own. Samples of the soluble organic fraction representing transient composites were submitted for bioassay over five tester strains, TA1535, TA1537, TA1538, TA98 and TA100.

All five tester strains are histidine-dependent cells by virtue of mutations within the histidine functional genetic unit. When these histidine-dependent cells are grown on minimal medium agar plates containing a limited amount of histidine, only those cells that revert to histidine independence are able to form colonies. The trace amount of histidine allows all the bacteria plated to undergo a few divisions, which is essential for mutagenesis to occur. It is these histidine-independent revertants which are scored as colonies against a slight background growth consisting of histidine-requiring cells that have depleted the histidine present within the minimal medium.

In addition to mutations in the histidine functional genetic unit, all the tester strains have a defective lipopolysaccharide coat which allows large molecules to permeate the bacterial wall, thus increasing bacterial sensitivity to mutagenic aromatic compounds. Furthermore, a UV mutation decreased bacterial sensitivity to additional mutagenic agents. TA1535 and its plasmid-containing counterpart, TA100, detect base pair substitutions; while TA1537 (and TA1538 with its plasmid-containing counterpart, TA98) respond to frameshift mutagens. The plasmids present in TA98 and TA100 are believed to cause an increase in error-prone DNA repair leads to more mutations. Thus, the five tester strains in tandem provide a very sensitive method for the detection of potentially mutagenic environmental samples.

Table 22 summarizes the results in revertants per microgram of extract. In most cases, the two EDS blends, EM-482-F and EM-485-F, exhibited the

TABLE 22. SUMMARY OF AMES BIOASSAY ANALYSIS OF ORGANIC SOLUBLES FROM PARTICULATE MATTER COLLECTED DURING FTP

Fuel Code	Description	RLI-16 Activation	Model Predicted Mean Slope, revertants/µg extract				
			TA-1535	TA-1537	TA-1538	TA-98	TA-100
EM-329-F	base DF-2	No	0.5	1.9	3.7	6.0	17.1
		Yes	0.1	1.4	3.5	3.1	7.2
EM-453-F	shale diesel marine	No	0.5	4.3	6.6	12.0	30.5
		Yes	0.1	4.8	11.0	6.3	14.5
EM-473-F	Paraho JP-5	No	0	4.8	6.8	5.5	14.3
		Yes	0.2	1.9	10.3	4.0	5.7
EM-474-F	Coal Case 5A	No	0	5.8	8.3	13.2	23.8
		Yes	0.1	4.0	8.7	5.2	20.7
EM-476-F	Broadcut	No	0	5.5	9.6	13.4	44.6
		Yes	0.2	4.2	10.6	5.0	14.2
EM-478-F	25% SRC-II	No	0.6	6.3	10.0	10.4	61.3
		Yes	0.1	7.0	12.0	5.3	13.7
EM-482-F	25% EDS	No	0.1	12.5	11.4	24.3	19.7
		Yes	0.2	8.2	10.9	8.8	16.3
EM-485-F	25% EDS naphtha	No	0	13.2	18.5	19.8	17.4
		Yes	0.1	12.2	16.2	9.0	8.6

greatest number of revertants per microgram of extract for strains TA1535, TA-1537, TA-1538, and TA-98. This relationship occurred whether or not metabolic activation was applied. Results for strain TA-100 without activation indicated that the 25% SRC-II and the Broadcut fuel were associated with the greatest number of revertants per microgram. Once metabolically activated, the extracts from the 25% SRC-II and the Broadcut fuel tests acted much like those from the 25% EDS, Coal Case 5A, and shale diesel marine evaluations. It is interesting to note that the TA-100 strain responded equally to both the 25% EDS naphtha blend and the base DF-2.

A comparison of "distance specific" Ames activity is shown in Table 23. These data take into account the particulate rate and percent organic extractables from each fuel blend, resulting in Ames activity as revertants per kilometer. Data in this form indicate that the base DF-2 and the Paraho JP-5 generally yielded lower Ames responses than the other fuels for all five strains. Strain TA-100 without metabolic activation indicated that the 25% SRC-II blend and the Broadcut blend were associated with the most revertants per kilometer. Once activation was applied, the revertants were reduced to approximately the same levels as those for some of the other blends. In the majority of cases, metabolic activation reduced Ames activity on all 5 strains. This trend implies that the organic soluble portion of the particulate matter from the fuels tested probably contained direct-acting mutagens as well as indirect-acting mutagens.

The Paraho JP-5 fuel, EM-473-F, was associated with the greatest fluorescence response during the transition period on the HPLC polarity profile, and twice the level of BaP generated with the base DF-2 fuel. It was anticipated that the Paraho JP-5 would show high Ames response, based on a CRC study[15] and the fact that BaP is a known mutagen; but the Ames data did not support this supposition. The greatest Ames response was associated with the 25% SRC-II and the Broadcut on strain TA-100. Samples generated using two blends also had much higher HPLC ultraviolet responses at both 8 and 38 minutes, as compared to the other blends. The 25% EDS sample also had a high peak at 38 minutes, but no response at 8 minutes. At 8 minutes, in the nonpolar region, BaP and similar PNA compounds elute. Broadcut fuel was associated with higher BaP emissions than base fuel, while the 25% SRC-II did not. It is possible that some of these fuels emitted organics which contained PNA's and possibly BaP isomers that were not detected in the BaP analytical procedure, but were seen in the HPLC polarity profile and also caused high Ames responses.

TABLE 23. SUMMARY OF AMES BIOASSAY RESULTS IN REVERTANTS PER DISTANCE DURING FTP

Fuel Code	Description	RLI-16 Activation	Model Predicted Mean Slope, 10^3 revertants/km[a]				
			TA-1535	TA-1537	TA-1538	TA-98	TA-100
EM-329-F	base DF-2	No	18	70	135	219	624
		Yes	4	51	128	113	263
EM-453-F	shale diesel marine	No	24	204	313	568	1444
		Yes	5	227	521	298	687
EM-473-F	Paraho JP-5	No	0	177	250	202	525
		Yes	7	70	378	147	447
EM-474-F	Coal Case 5A	No	0	296	423	673	1214
		Yes	5	204	444	265	1055
EM-476-F	Broadcut	No	0	316	552	771	2564
		Yes	12	242	610	288	817
EM-478-F	25% SRC-II	No	34	365	580	603	3553
		Yes	4	406	696	307	794
EM-482-F	25% EDS	No	5	620	566	1206	978
		Yes	10	407	541	437	809
EM-485-F	25% EDS naphtha	No	0	486	681	729	641
		Yes	4	449	597	331	316

[a]Calculation incorporates particulate mass rates based on 47mm Pallflex filters, percent organic solubles extracted from Pallflex "20 x 20" filters, and data in Table 21.

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